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8

SELECT METHODS
IN
CHEMICAL ANALYSIS

(CHIEFLY INORGANIC)

BY



WILLIAM CROOKES, F.R.S., V.P.C.S.

EDITOR OF 'THE CHEMICAL NEWS'

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PREFACE

TO

THE SECOND EDITION.

THE first edition of *Select Methods in Chemical Analysis* is exhausted, and the multitude of new methods which have been introduced into laboratory practice renders it necessary that the work should be not merely revised, but to a great extent rewritten. In submitting the new edition to the chemical world there are a few points to which attention must be called. It has not been desired to produce an encyclopædia of chemical analysis, in which is laid down every good method for the qualitative and quantitative examination of every known substance under every possible combination of circumstances. Many processes and operations have been omitted as universally known, and many others as being untrustworthy, or at least doubtful. The Author has merely given such methods as have been proved in his own laboratory. Others—possibly no less efficient—have been passed over because he cannot vouch personally for their value. A main object has been to bring into notice a number of little-known expedients and precautions which prevent mistakes, insure accuracy, and economise time.

The arrangement of the book has been adopted, not without careful consideration, as the one which necessitated the smallest number of back references.

LONDON: Nov. 1885.

PREFACE

TO

THE FIRST EDITION.

It will be perceived from the title of this work that the Author has not intended to provide the student with a complete text-book of analysis, but rather with a laboratory companion, containing information not usually found in ordinary works on analysis. The Author has tested most of the new processes which have appeared during the last twelve years in the 'Chemical News'; and as some of these have proved to be of great value, it was thought that a service would be rendered to analytical chemistry if these trustworthy methods of analysis were systematically arranged in a convenient form for laboratory use. In some instances the descriptions are given in the language of the original writer, but in all cases where the Author has improved the processes the necessary modifications have been introduced.

It is strange that modern works on analysis should ignore about twenty of the elements. Even Fresenius gives only a separate form for their detection. Were investigators more in the habit of looking for the 'rare' elements, they would no doubt turn up unexpectedly in many minerals. In the present work equal prominence is given both to the rare and to the ordinary elements.

The order in which the analytical separation of the metals is carried out will be readily understood. Take, for instance, the case of copper. After giving the best method for the detection and quantitative estimation of this metal, comes a description of the processes for separating it from those metals which have been

previously passed under review, as mercury, silver, and zinc ; but no attention is paid to the separation of copper from such metals as lead, tin, &c., which have not previously been treated of. Under the respective headings 'Lead' and 'Tin,' the separation of these metals from copper is described.

A complete list of separations has not been attempted. Where no process of separation or estimation is given, it may be inferred that the Author has had no experience in any but the well-known methods employed in most laboratories ; and to have introduced these ordinary processes into the work, simply for the sake of filling up gaps, would have largely increased its bulk without adding materially to its value. To save space, the description of a process is frequently discontinued at the point where the substances under separation are brought to such a state that the concluding steps are obvious.

No special system of weights and measures has been employed ; many of the descriptions having been condensed from the original memoirs, it was thought better to retain the system therein adopted, so as to have simple numbers to deal with, instead of having to convert them to one common scale and to introduce decimals. Thus, when an author says, take 8 grains of a substance, 0.51816 gramme has not been substituted ; and where 10 grammes are mentioned, he has not put 154.3840 grains. When not otherwise expressed, all degrees are according to the Centigrade scale. Formulæ have been avoided as far as practicable.

The names of discoverers of really novel or valuable processes are mentioned ; but the introduction in a laboratory guide-book of the name of everyone who has contributed some trifling modification of a process would materially interfere with the concise description of the various methods, and, as a rule, such names have been omitted.

Some processes of great historic interest, as Professor Stas's method for the preparation of pure silver by distillation and otherwise, have been given in considerable detail ; for this the Author thinks no apology is necessary, for it is always well for the student to have before him the highest models, in order that he may strive to attain a like perfection.

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SELECT METHODS IN CHEMICAL ANALYSIS.

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POTASSIUM, SODIUM, LITHIUM, CÆSIUM, RUBIDIUM, (AMMONIUM).

POTASSIUM.

A New Test for Potassium.

M. L. DE KONINCK finds that if a 10 per cent. solution of sodium nitrite is mixed with cobalt chloride and acetic acid, the liquid forms a reagent for the detection of potassium much more sensitive than platinum chloride. An immediate yellow precipitate is obtained in a solution containing one part potassium chloride in 100 parts of water. It is still perceptible if diluted to 1 : 1000, but in the proportion 1 : 2000 a precipitate is no longer obtained. Ammonia gives a similar but much less sensitive reaction ; magnesium, calcium, barium, strontium, iron, aluminium, and zinc salts are not precipitated by this reagent.

Estimation of Potassium.

Whenever possible, potassium should be estimated in the form of platinum salt. The results are exact and unvarying, and they are attended with the great advantage that, owing to the high atomic weight of platinum, any errors of manipulation, unless beyond the limits of probability, affect but slightly the percentage result of potassium. To obtain trustworthy results several precautions have to be attended to ; these have been fully described by Messrs. F. T. Teschemacher and J. Denham Smith, and the following process, which the author has verified on many occasions, is condensed from their description (*Chemical News*, xvii. 244).

It is assumed that the salt under examination is a sample of commercial potassium chloride, or that the alkalies exist in such a condition that, by the addition of hydrochloric acid in excess, they will be con-

verted into chlorides. Take 500 grains of the salt, previously carefully ground and mixed, and dissolve it in water, filtering if requisite, and washing the insoluble portion till solution and washings measure 5000 grains. Mix this solution by pouring from one glass to another, and take 500 measured grains of the liquid (measured accurately, always at one level of the eye and one level of liquid and line of measurement), dilute these 500 grains till they measure 5000 liquid grains and mix; 1000 measured grains of this solution contain 10 grains of the original salt.

Now, to 1000 measured grains of this solution, add excess, say 50 grains, of hydrochloric acid, if the alkalies are not present as chlorides, and pour into a shallow porcelain dish, making, with the rinsings of the measure, &c., some 1500 grains of solution. Heat the dish and contents nearly to ebullition, and add to the hot liquid so much solution of platinum chloride as is equal to 20 grains of the metal. Evaporate this mixture on the water-bath nearly to dryness; that is, to the point when the thick syrupy liquid, on the momentary removal of the dish from the bath, passes into an orange-coloured pasty mass. At this point remove the dish from the bath, and at the same instant, and before the dish and its contents have had time to cool, drench it with 500 to 600 grains of rectified methylated spirit, containing about 15 per cent. of water and 85 of alcohol; mix rapidly by imparting a rotatory motion to the contents of the dish; then cover it and allow it to digest for five minutes. Have a filter ready, not too small, of 400 to 500 grains capacity, in a funnel with a cover: wash the filter first with hot water, and then with spirit, and after a short digestion pour the alcoholic solution of the platinum salts on to the filter, draining the crystalline solid scales of the potassium salt as dry as possible, and again drench, agitate, and digest the insoluble salt with spirit; repeat this a third time, when the spirit will come away nearly colourless. Now collect the light orange crystalline scales of the potassium platino-chloride on the filter, by means of a wash-bottle, and, if need be, wash with spirit till it passes perfectly colourless. It is very advisable to wash the potassium platino-chloride by decantation, and finally by a stream of spirit from a wash-bottle, to avoid the use of stirrers so as to prevent the scales being broken down, and to keep both dish and funnel lightly covered till the washing is completed.

There is now nothing more to be done than to dry and weigh the potassium platino-chloride, and to ignite and weigh the filter and add this to the weight of the salt. Owing, however, to the crystalline nature of the salt thus obtained, but a slight stain adheres to the filter, so that the loss by ignition is very minute and does not affect the result. As this crystalline precipitate is not hygrometric, its weight is easily and accurately determined.

In this process the following points must be chiefly attended to:—

- I. Dilution of solutions.

II. Use of platinum chloride in large excess, about 20 grains of metallic platinum to 10 grains of the salt examined.

III. Heating of solutions, and evaporation so conducted as to obtain the potassium salt in a crystalline scale-like condition.

IV. Evaporation on water-bath to a pasty condition—no further.

V. Drenching with spirit whilst the salt and dish are hot, and instantly on removal from water-bath.

VI. Washing by decantation, and avoiding breaking down of the crystalline precipitate.

In practice, the process is a rapid one, from beginning to end requiring about two hours; less time, indeed, than is frequently expended in merely washing the dense pulverulent precipitate which is obtained by the usual mode of manipulation.

The results are very accurate. The authors take 244.20 as the equivalent of the potassium platino-chloride.

Many modifications of the above described process have been proposed.

It has been found that the determination of potash by platinum chloride is the more inaccurate the more foreign salts, such as sodium chloride, are present. The result obtained is generally too high, since the sodium platino-chloride, if it has become too dry, can no longer be entirely removed by washing with alcohol.

Precht conducts the determination of potassium as follows:—The sulphuric acid is removed by barium chloride in a solution containing 0.5 of hydrochloric acid to 1 of the salt. The clear liquid should contain neither barium chloride nor sulphuric acid. Traces of the latter may be removed in the measuring vessel by finely pulverised barium chloride. Small quantities of sulphuric acid are admissible if the solution with platinum chloride is not evaporated quite to dryness. In acid solutions the objection to the removal of sulphuric acid by means of barium chloride, viz. that alkalies are carried down along with the barium sulphate, has little foundation.

In neutral solutions so much potassium sulphate is thrown down that an error of 1 per cent. may be occasioned. In evaporating down with platinum chloride care should be taken that large crystals of sodium platino-chloride are not formed, which would interfere with washing. The latter process is best performed with hot alcohol, there being no danger of the reduction of the platinum. A mixture of alcohol and ether is not to be recommended, nor an addition of glycerine. For the determination of small quantities of potassium chloride along with an excess of sodium chloride, Precht evaporates 10 to 100 grammes along with a solution of sodium platino-chloride of known strength. The potassic salts are thus thrown down, the excess of the sodium compound is washed away with the absolute alcohol, the platinum reduced on the filter and weighed.

The committee appointed by the chemical section of the British

Association reports that (1) potassium in the form of pure chloride can be determined with great accuracy by precipitation as platino-chloride. If a large excess of platinum solution be employed, and alcohol only used for washing the precipitate, the results have a tendency to exceed the truth. By avoiding the use of a large excess of platinum solution more accurate results are obtained. If a small volume of platinum solution be employed in the first instance for washing the precipitate (as recommended by Tatlock), and the washing then completed with alcohol in the usual way, the results are very accurate. Potassium platino-chloride appears to be practically insoluble in a concentrated solution of platinum chloride.

(2) In presence of a considerable proportion of sodium chloride, washing the precipitate with alcohol alone, tends to give results in excess of the truth. If the precipitate be first treated with platinum solution the results are somewhat low, apparently owing to the solubility of the precipitate in solutions of sodium platino-chloride; the error increases with the amount of sodium, but is never very large, and a correction may be applied if desired.

(3) If Tatlock's method be employed, there is no occasion to separate any sulphates, nitrates, or magnesium; but if the amount of chloride present is insufficient for the existence of all the potassium as potassium chloride, the deficiency must be supplied by the addition of sodium chloride or hydrochloric acid. The results obtained are in many cases very accurate, but have a tendency to be somewhat below the truth.

(4) There is practically no advantage in drying potassium platino-chloride at 180° C. rather than at 100° C.; the loss at the higher temperature was found to exceed 0.07 per cent. of the weight of the precipitate, but is probably governed by the conditions of precipitation.

(5) The committee is of opinion that a preliminary washing of the precipitate of potassium with a solution of platinum chloride is a valuable modification of the usual process. As the method so modified is capable of direct application to the commercial potassium salts, and does not necessitate the removal of sulphates, nitrates, or magnesium, the committee considers that it deserves to be generally applied to the determination of potassium in commercial products containing it.

Mr. R. Tatlock's modification of the platinum process above referred to is as follows:—Dissolve 35 grammes of the sample in water, filter if necessary and make up the bulk to 500 c.c. Deliver 10 c.c. of the solution into a small porcelain basin, add 20 c.c. of water, stir, and then add 30 c.c. of a solution of platinum chloride containing 7 grammes of metallic platinum in every 100 c.c. Evaporate on water-bath, but not to perfect dryness. Add a few drops of water and evaporate again; remove the basin and stir the precipitate well with 2 c.c. of the platinum solution; then wash the precipitate on the filter with 1 c.c. more. Now wash the basin and filter and contents with

the smallest possible quantity of alcohol of 95 per cent. Dry the filter containing the precipitate on the water-bath; remove the precipitate as completely as possible into a small platinum capsule; dry at 100°C . and weigh. Ignite the filter with trace of adhering precipitate; weigh the residue of $\text{Pt} + 2(\text{KCl})$ which is left; calculate its weight of $2(\text{KCl})\text{PtCl}_4$, and add the weight to that of the precipitate already obtained.

The process employed at Leopold's-hall and Stassfurt is described by Drs. Zuckschwerdt and West as follows:—10 grammes of a well-mixed sample are dissolved in a 500 c.c. flask filled up to the mark, shaken, an aliquot part filtered, and 20 c.c. (= 0.4 gramme) measured off. This is mixed in a porcelain capsule with 7 c.c. of a solution of platinum chloride, containing 10 grammes of platinum in 100 c.c.

As commercial samples rarely contain more than 20 per cent. of sodium chloride, whilst the above quantity of platinum would suffice for 0.4 gramme of sodium chloride at 100 per cent., there is always a considerable excess of platinum chloride present.

The contents of the capsule are then evaporated on the water-bath with frequent stirring to the consistence of syrup, so that when cold the mass appears dry. The free hydrochloric acid is thus chiefly expelled. When cold the mass is covered with 10 c.c. of alcohol at 95 per cent., well rubbed up with a glass rod, and the washings are poured upon a balanced filter. Alcohol is again spirted on in smaller quantity; the mass is again rubbed up, the washings poured off, and the operation is repeated once more. As a rule, at the second decantation the colour of the washings, and consequently the proportion of the platinum double salt, will be very slight, and in the third operation it disappears altogether; otherwise the operation must be repeated once more. The precipitate, which now consists of perfectly pure potassium platino-chloride, is brought upon the filter by means of the alcohol washing-bottle; and after drying for half an hour at 110° to 115° , it is weighed under the same conditions as it had been when empty.

The total quantity of alcohol consumed is in general 50 c.c. The errors fall within the narrowest limits of permissible experimental errors, and could scarcely be removed or avoided by greater complication.

MM. Corenwinder and G. Coutamine add to the portion taken for analysis a slight excess of hydrochloric acid, and then, without taking any notice of the possible presence of sulphuric acid, silica, or phosphoric acid, they evaporate in the water-bath, after having added a sufficiency of platinic chloride. The potassium platino-chloride thus obtained is digested with alcohol at 95° , mixed with ether, and washed in the ordinary way with the same liquid. When this operation is complete, boiling water is poured upon the filter by means of a pipette, till the platino-chloride is entirely dissolved, and the filtered liquid is collected. Water containing sodium formiate is then heated, and whilst it is boiling the preceding solution of potassium platino-

chloride is carefully poured into it by degrees. In a few moments the platinum is thrown down as a black powder, which merely needs to be washed, dried, heated to redness, and weighed in order to find the quantity of potash present in the sample.

Dr. F. Mohr estimates potassium by titrating the chlorine contained in the platino-chloride. He decomposes this salt by fusing it in a platinum crucible, with twice its weight of sodium oxalate. After lixiviation the chlorine is determined by a decinormal silver solution.

M. L. de Koninck throws down potassium with the ordinary precautions by platinum chloride; the precipitate is collected on a filter, washed in alcohol, and immediately dissolved in boiling water. The solution is reduced hot by magnesium. All the chlorine of the platino-chloride is obtained in the form of a soluble chloride and a black precipitate of reduced platinum. At the same time the magnesium decomposes the water, yielding hydrated magnesia with an escape of hydrogen. When the reduction is complete the mixture is filtered, and in the neutral solution the chlorine is determined in the usual manner with a standard solution of silver nitrate, using potassium chromate as indicator.

The following processes are based upon different reactions :—

Estimation of Potassium Sulphate.

Dr. West finds that the ordinary method of removing the sulphuric acid by means of barium chloride and converting the excess of the latter into barium carbonate by evaporation and ignition with oxalic acid, is open to a double objection. Barium sulphate retains much potassium chloride, even in an acid solution, and during the ignition a further quantity of barium chloride is lost by volatilisation. At Stassfurt the following method is in use :—10 grammes of the salt in question are placed in a 500 c.c. flask with 350 to 400 c.c. of water and 25 c.c. of hydrochloric acid at 25 per cent., and a solution of barium chloride (almost saturated and containing 50 c.c. aqueous hydrochloric acid per litre) is gradually added, boiling up each time till the sulphuric acid is entirely thrown down, a point easily reached with practice. A very small excess of sulphuric acid has no effect upon the result, whilst an excess of barium chloride increases the result; or the sulphuric acid in the salt may be determined volumetrically in a separate portion with barium chloride and potassium chromate, and the quantity of barium chloride thus found is added to the potassium salt in an acid solution. In evaporating, care must be taken that the free hydrochloric acid is entirely expelled, which is not easy in presence of much magnesia, otherwise an error may arise of 0·5 per cent. The correction for the potassium chloride retained by the barium sulphate is as follows : in 10 grammes of potassium sulphate there are 4·59 sulphuric anhydride = 13·79 grammes barium sulphate,

which occupy the space of 3 c.c. Each c.c. of the precipitate contains as much potassium as 6 c.c. of the solution.

Estimation of Potassium by Means of Perchloric Acid.

Armand Bertrand finds that if the substance in question contains an ammoniacal salt the ammonia must be expelled by boiling with a little caustic lime. The solution should be perfectly clear. The filtered solution of the sample is evaporated on the water-bath in a small porcelain capsule with 5 c.c. of perchloric acid at 45° B., until the volume of the liquid is reduced to about 10 c.c. The capsule is taken off the water-bath, alcohol at 95 per cent. is added: it is let cool, and the potassium perchlorate is collected on a small filter. The precipitate is washed with alcohol at 95 per cent., containing 10 per cent. by volume of perchloric acid, until the liquid running through no longer shows the reactions of sulphuric and perchloric acids. The washing is then completed with alcohol at 95 per cent. without the admixture of perchloric acid. It is then dried in the stove. At the end of from twenty to thirty minutes the precipitate is detached from the filter and spread out on a tared watch-glass. It is heated and weighed twice to be certain that the desiccation is complete, and the weight of the potassium perchlorate thus obtained is noted. On the other hand, as there always remains a little perchlorate adhering to the filter, instead of using a tared filter, the author considers it more expeditious to operate as follows:—During the desiccation of the perchlorate in the watch-glass the filter is burnt in a platinum capsule, fitted with a lid. The potassium chloride, resulting from the calcination, is washed into a glass, and the chlorine is determined with a centinormal silver solution. A multiplication indicates the perchlorate to be added to that which has been weighed. This process gives accurate results in presence of lime, magnesia, soda, baryta, iron, alumina, and sulphuric or phosphoric acids, free or combined.

The author prepares his perchloric acid as follows:—He dissolves purified barium chlorate in lukewarm water, and precipitates with dilute sulphuric acid. He lets settle, draws off the clear liquid with a syphon, and washes the precipitate of barium sulphate. The solution of chloric acid is evaporated in a porcelain capsule over a naked fire until the concentrated liquid becomes yellow and emits a peculiar sound if heated further. It is then divided in capsules of 19 centimetres in diameter, each capable of containing about 700 c.c., and the evaporation is continued until the liquid is completely colourless and emits dense white fumes. In order to diminish the inevitable loss of perchloric acid a little water may be added from time to time during the concentration. Four parts of barium chlorate yield, in general, 1 part of perchloric acid at 45° B. The colourless liquid is distilled in a retort heated in a sand-bath. A long-necked tubulated receiver is adapted to the retort without the use of a cork.

Another process for the estimation and detection of potassium has been devised by M. A. Carnot.

He makes use of a reaction of potassium salts in a solution mixed with alcohol, in presence of sodium thiosulphate and a bismuth salt.

Dissolve in a few drops of hydrochloric acid 1 part of bismuth subnitrate—say half a gramme—and on the other hand about 2 parts (1 gramme to $1\frac{1}{2}$) of crystallised sodium thiosulphate in a few c.c. of water. The second solution is then poured into the first, and concentrated alcohol is added in large excess. This mixture is the reagent.

If brought in contact with a few drops of the solution of a potassium salt, it at once gives a yellow precipitate. With an undissolved potassium salt it produces a decidedly yellow colouration, easily recognised.

All potassium salts with mineral acids are equally susceptible of his reaction, sulphates and phosphates as well as nitrates, carbonates, chlorides, &c. It is also very sensitive with the organic salts, tartrates, citrates, &c.

The reaction is not interfered with by the presence of other bases, with which nothing analogous is produced. The character is, therefore, perfectly distinct.

Baryta and strontia alone may occasion some difficulty, by reason of the white precipitates of double thiosulphates which they form with the same reagent, but it is very rare to meet them along with potash, and they are very easily detected and removed.

If we have a solution containing merely a few milligrammes of potash, it is reduced by evaporation to a very small volume, or even to dryness, when the characteristic reaction readily appears. Or slips of filter-paper may be repeatedly saturated with the dilute solution, and after drying be steeped in the alcoholic reagent, when the yellow colour will appear, especially on the margins of the paper.

The author's quantitative experiments refer chiefly to nitrates, chlorides, and mixtures of the two salts. With some special precautions the method may probably be applied directly to sulphates, though these are easily converted into chlorides by barium chloride, removing the excess of barium with sodium or ammonium carbonate.

The thiosulphate of commerce is sufficiently pure for use; the crystals are dissolved in a small quantity of water at the moment of the experiment.

The bismuth chloride is prepared by treating the pulverised metal with a few drops of nitric acid, evaporating to dryness, and then heating with a very small quantity of hydrochloric acid. The lead possibly present in the bismuth is got rid of by adding to the cold solution concentrated alcohol, which causes lead chloride to be deposited. Or bismuth subnitrate may be dissolved in a few drops of hydrochloric acid.

The liquid in which the potassium is to be determined should not exceed 10 to 15 c.c. in bulk, so that the entire volume of the aqueous

solution may not exceed 20 to 25 c.c. For 1 part of supposed potash we take 2 parts of bismuth or $2\frac{1}{2}$ of subnitrate with 7 parts of crystalline thiosulphate.

The solution of the potassium salt is placed in a small flask, the bismuth solution is added, then the thiosulphate; the whole is mixed rapidly, and 200 to 250 c.c. of concentrated alcohol are added. The whole is agitated for a few moments and left to settle. The yellow precipitate collects at the bottom of the flask, and may be filtered after a quarter of an hour, and carefully washed with alcohol.

The precipitate cannot be weighed; it is dissolved upon the filter in excess of water; the bismuth is thrown down as sulphide by ammonium sulphide, washed by decantation, collected on a tared filter, dried at 100° , and weighed. The weight obtained may be corrected by separating from the filter a part of the dried precipitate and heating it again to 150° to 200° in a small platinum crucible, weighing before and after, and correcting the total weight of the sulphide accordingly. The weight of the potash is found on multiplying the weight of the bismuth sulphide found by 0.549. The method has been found accurate in presence of soda, lithia, ammonia, lime, magnesia, alumina, and iron.

The author finds on the same reaction the following volumetric process:—It consists in determining, by means of a standard solution of iodine, the proportion of thiosulphuric acid in an aqueous solution of the same salt. The iodine solution employed is decinormal, as recommended by Prof. Mohr; 12.7 grammes of pure iodine being dissolved in water by the aid of about 18 grammes of potassium iodide, and the solution made up to 1 litre. The solution of calcium thiosulphate contains, per litre, 200 grammes of the crystalline salt. The solution of bismuth contains, per litre, about 100 grammes subnitrate and a sufficient proportion of hydrochloric acid and alcohol. For each operation, 1 gramme of the salt to be analysed is taken, or a quantity which may contain at most 70 centigrammes potash, and it is dissolved in about 10 c.c. of water. If the salt contains much sulphate, calcium chloride is added (1 gramme of this salt dissolved in water, or a corresponding quantity of pure calcium carbonate dissolved in hydrochloric acid is fully sufficient for 1 gramme of sulphate), and the mixture is left for a few moments in order that the calcium sulphate may have time to precipitate. Into the same flask are poured successively 10 or 20 c.c. of the solution of bismuth, according as the quantity of potash is presumably below or above 30 centigrammes; an equal volume of the calcium thiosulphate is next added; and lastly, pour 100 to 150 c.c. of concentrated alcohol. The whole is well stirred up and left to settle for a quarter of an hour. The precipitate of double thiosulphate, whether mixed with calcium sulphate or not, is collected on a filter and carefully washed with alcohol. The funnel is then set over a flat-bottomed flask and cold water is poured upon it with a washing-bottle, when the thiosulphate dissolves rapidly.

The portion of calcium sulphate which may dissolve at the same time does not interfere with the subsequent operations. A little clear starch paste is then added to the solution, and a few c.c. of hydrochloric acid. The standard iodine liquid is then added with a burette until a deep brown tint appears in the liquid. The volume of the iodine solution employed is then read off, and the weight of the potash is thence calculated.

Volumetric Estimation of Potassium.

E. Burcker has examined the two existing processes. In one of these the potassium is thrown down as cream of tartar by means of a solution of sodium bitartrate. The precipitate is then washed on the filter with a solution of potassium bitartrate saturated in the cold, in order to remove the excess of soda, then dissolved in hot water, and determined alkalimetrically with normal soda. In the modification proposed by Marchand, after having prepared a standard solution of sodium bitartrate, each c.c. of which corresponds to 1 centigramme of potash, the potash is precipitated by means of an excess of this solution, and the excess added is determined by means of a standard alkali. The author finds that the direct method is preferable, being not only more exact but more rapid. The presence of sodium and magnesium salts does not interfere, but calcium salts should be previously eliminated.

Precipitation of Potassium as Fluosilicate.

In some cases it is preferable to precipitate the potassium in the form of fluosilicate. This is usually effected by the addition of hydrofluosilicic acid. A great improvement on this plan has been proposed by Drs. Knop and Wolf, who employ fluosilicate of aniline as the precipitant for potassium.

To prepare this reagent, dilute the aniline with twice its volume of alcohol at 80° to 90°; then add an equal volume of saturated fluosilicated alcohol. The liquid first becomes heated, and then almost immediately solidifies. Spread the mass in a capsule, dry in the air, and reduce to powder.

The powder is composed of the desired fluosilicate, and of all the silicic acid produced during the reaction. The acid being in its insoluble modification, one washing in water suffices to separate the soluble aniline fluosilicate from the inert silica which remains on the filter.

If coloured aniline is used, the powder must be previously washed in ether, which dissolves only the colouring matter.

Aniline fluosilicate crystallises in nacreous scales. Soluble in water, insoluble in alcohol and ether, this salt is very useful in separating potassium from sodium, and even from ammonium, provided the liquid does not contain much excess. When this is the case the ammonia or its saline combination must first be expelled by heat.

In using this reagent, the salts are first acidulated by hydrochloric acid. Absolute alcohol is then added. On addition of an aqueous solution of aniline fluosilicate the potassium is thus precipitated in the state of fluosilicate, even in presence of phosphoric acid.

SODIUM.

Analysis of Salt-Cake.

The method preferred for the examination of salt-cake, black-ash, soda-ash, and other commercial products of the alkali manufacture, is that given by Dr. C. R. A. Wright, F.R.S. Ordinary salt-cake is valued according to the percentage of available sodium sulphate contained; i.e. the percentage of sodium sulphate existing mainly as such, and partly as sodium bisulphate. The mode of estimation of the available sulphate usually pursued is the following:—

1. The sodium chloride is determined volumetrically by a standard silver solution.

2. The quantity of a standard alkaline solution required to render a known weight of salt-cake exactly neutral to test papers is determined, and the result sometimes calculated as anhydrous sulphuric acid, sometimes as monohydrated sulphuric acid, called 'free acid.'

8. The difference between the sum of the two previous determinations and 100 is assumed to be 'available sodium sulphate.'

By this mode of proceeding errors of one to three or more per cent. are introduced; ordinary salt-cake containing, in addition to sodium sulphate, bisulphate and chloride, perceptible quantities of lead sulphate, iron persulphate, iron sesquioxide, calcium sulphate, magnesium sulphate, moisture, and particles of sand, brick, &c., derived from the furnace during the manufacturing processes. Where a greater degree of accuracy is desirable, a known weight of salt-cake may be treated with water, ammonia and ammonium oxalate added to the unfiltered solution, and the precipitated iron sesquioxide and calcium oxalate, with the insoluble matters, weighed after ignition: by moistening the ignited precipitate with pure sulphuric acid, and igniting again, the calcium oxalate is converted into calcium sulphate, and then the weight of the mixed substances indicates all the 'impurities' present in the salt-cake; with the exception of the magnesium sulphate, which rarely amounts to more than traces, and the moisture, which is occasionally a very perceptible quantity, especially in samples that have been made some length of time.

The amount of iron persulphate present depends on the degree of heat to which the salt-cake has been subjected during manufacture. In highly-roasted samples, cold water yields a solution containing no iron whatever, all the iron present in the salt-cake consequently existing as sesquioxide; specimens of under-roasted salt-cake, on the other hand, when treated with cold water, leave only fragments of brick,

calcium sulphate, &c., undissolved, all the iron existing as persulphate. In ordinary salt-cake, however, there is so little ferric sulphate that no perceptible error is committed in assuming that all iron present exists as sesquioxide, and all the 'free acid' as sodium bisulphate. Accordingly, the following methods have been found to give tolerably expeditiously the exact composition of such salt-cake:—

(a.) A known weight, 5 or 10 grammes, is dried at 110° — 120° C., till constant in weight; too great elevation of temperature being avoided to prevent any possible loss of hydrochloric acid by reaction of the sodium bisulphate on the sodium chloride present.

(b.) The sodium chloride is determined volumetrically by a standard silver solution.

(c.) A solution of sodium hydrate free from carbonate, or of caustic ammonia, of known strength, is added to a known weight of salt-cake until test-papers indicate exact neutrality of the liquid; the alkaline solution used accordingly corresponds to the iron persulphate and sodium bisulphate together, and may therefore be safely calculated as the latter.

(d.) A known weight of salt-cake is boiled with an excess of a standard sodium carbonate solution, and filtered; the unneutralised alkali is then determined by a standard acid solution. The amount of alkaline solution neutralised by the salt-cake indicates the calcium sulphate, sodium bisulphate, and iron persulphate together; and hence the difference between (c) and (d) indicates the calcium sulphate. Or the calcium sulphate may be determined gravimetrically by precipitation with ammonium oxalate, after separation of the iron sesquioxide by ammonia from the solution of a known weight of salt-cake in hydrochloric acid.

(e.) The precipitate thrown down in (c) may be collected and boiled with hydrochloric acid; the insoluble sand, &c., may be weighed, and the ferric salt reduced by zinc or other reducing agent, and titrated volumetrically by permanganate or otherwise.

(f.) When the lead sulphate is to be determined, it may be done by treating a considerable quantity, say 20 grammes, with water, and boiling the insoluble residue with strong hydrochloric acid till the lead sulphate is entirely dissolved; from this solution lead sulphide may be thrown down by sulphuretted hydrogen, and the lead determined in the ordinary way.

(g.) If magnesium sulphate is to be determined, it may be done by dissolving a known weight, say 20 grammes, in hydrochloric acid, adding ammonia and ammonium oxalate, and precipitating the magnesium from the filtrate by a phosphate, and ultimately weighing the magnesium pyrophosphate.

(h.) If the preceding determinations have been carefully conducted, the difference between 100 and the sum of them may be safely taken as sodium sulphate; if this is to be directly determined, however, it may

be done either by determining the total sulphuric acid present by dissolving a known weight of salt-cake in hydrochloric acid, and precipitating by barium chloride, and weighing the barium sulphate; subtracting the sulphuric acid, contained as calcium sulphate, sodium bisulphate, magnesium sulphate, and lead sulphate, the remainder being calculated as sodium bisulphate; or by adding ammonia and ammonium oxalate to the aqueous solution of a known weight, and estimating the residue left on evaporation of the filtrate and ignition with sulphuric acid; on subtraction from this of the amounts due to magnesium sulphate, sodium chloride, and sodium bisulphate, the sodium sulphate is directly ascertained.

The total 'available sodium sulphate' is known by adding $\frac{1}{12} \cdot 10$ of the sodium bisulphate to the amount of sodium sulphate found.

Mr. W. Tate proposes the following method for the analysis of salt-cake:—The free sulphuric acid and undecomposed salt are determined by standard solutions of sodium carbonate and silver nitrate respectively; calcium sulphate by ammonium oxalate; silica, and iron peroxide, by precipitation by ammonia or sodium acetate; and moisture, by drying at 100° C.

Another method, which is favoured by the 'high' analyst, differs from the above, inasmuch as the 'free acid and moisture' are estimated together by the loss of weight on ignition or roasting of a sample. Now it is clear that the result of ignition must be that a portion of the free sulphuric acid will react on part of the salt, forming sodium sulphate and liberating chlorhydric acid. Thus the analyst performs a manufacturing operation in the process of his analysis, and his 'results' represent a higher percentage of sodium sulphate than is really present in the original sample. And the amount of his error varies with the composition of the sample.

See also Dr. Grossmann's process for the 'Alkalimetric Determination of Sulphates.'

Black-Ash.—Commercially, the only valuable ingredient is the sodium carbonate, the amount of which is generally determined by lixiviation of a known weight of black-ash, and titration, by normal test acid, of the liquor obtained. In manufacturing establishments it is frequently the practice to lixivate the ash with water at some definite temperature, considered to be about the average temperature of the lixiviating vats; the liquor so obtained is examined (a) for alkali, determined by test acid; (b) for sodium sulphate, generally estimated roughly, but with sufficient nearness for manufacturing purposes, by addition of a standard barium chloride solution to a portion of the acidulated lixivate, till no further precipitate is thrown down; (c) for sulphide, estimated by passing chlorine through the alkaline lixivate till all sulphide is destroyed; boiling with hydrochloric acid, and volumetric determination of the sulphate as before, the increased amount representing the sulphide. Prizes are frequently given to

those workmen who produce black-ash containing but little sulphate, showing a nearly complete decomposition of the salt-cake employed; and occasionally prizes are given when the sulphate after oxidation is low in amount, it being supposed that this indicates that over-roasting of the black-ash has not occurred. A slight misapprehension, however, usually attends this mode of analysis; although an over-roasted black-ash will yield a perceptible quantity of sulphide when treated with nearly absolute alcohol, yet the fact of an aqueous solution containing sulphide by no means proves that the ash was over-roasted, inasmuch as, on addition of water to black-ash, there is always a mutual reaction between the calcium sulphide and sodium carbonate contained therein; the amount of sodium sulphide formed depends on the temperature and dilution of the liquid, and the time employed; and accordingly it is often found that the sulphide existing in the black-ash lye from the vats is very different in amount from that calculated from the laboratory analyses of the black-ash worked. The laboratory test for 'sulphate after oxidation,' therefore, is really useless, as it neither denotes the quality of work done by the furnace-man nor that of the black-ash lye.

In ordinary black-ash a sodium compound is contained¹ insoluble in hot water, even on long digestion, but decomposable by long-continued boiling. In cases, therefore, where the total 'available alkali' is to be exactly determined, either this long boiling must be performed or the total sodium present must be determined gravimetrically, and that contained as chloride and sulphate subtracted; in either case a tedious operation. The same applies in the case of the analysis of the lixiviated black-ash, or vat-waste. Ordinarily, the vat-waste is examined by lixiviating or washing on a filter a known weight of waste fresh from the vats, or previously completely dried. In either case a considerable amount of calcium sulphide comes into solution, and hence if the solution so obtained be immediately titrated with test acid, more sodium is indicated as present than really has been dissolved out. By passing carbonic acid through the solution till sulphuretted hydrogen is completely expelled, boiling to decompose calcium bicarbonate, and filtration from the precipitated calcium carbonate, this error is avoided. The same effect is produced by adding ammonium carbonate to the solution, and boiling in a flask till no further evolution of ammoniacal gases takes place; but in either case the sodium contained in the insoluble compound, or as sulphate (found by oxidation of calcium sulphide and subsequent reaction on the sodium carbonate, especially if the waste have been previously dried), remains unestimated. When accuracy is required, therefore, a gravimetric determination of sodium is unavoidable.

In cases where an accurate analysis of the total contents of a sample of black-ash is required, the following method gives reliable results

¹ *Chem. Soc. Journ.* xx. 407.

tolerably speedily. Most of the modes of determination are likewise applicable to samples of dry vat-waste:—

(a.) A known weight is dissolved in hydrochloric acid, the insoluble coke and sand collected on a weighed filter, and the carbon subsequently burnt off.

(b.) In the filtrate from (a) the sulphuric acid is estimated by precipitation by barium chloride and weighing the barium sulphate.

(c.) A known weight is dissolved in nitric acid, and the chlorine determined volumetrically by a standard silver solution.

(d.) A known weight is treated in Mohr's carbonic acid apparatus; the ammonium carbonate formed is precipitated by boiling with calcium chloride, the precipitate washed till the washings are neutral, dissolved in a slight excess of standard hydrochloric acid, and the excess determined by a standard alkaline solution; thus the carbonic acid can be calculated.

(e.) A known weight is fused with four times its weight of a mixture of three parts dry sodium carbonate and one of potassium nitrate (both free from sulphate). From the total sulphate thus formed, and estimated gravimetrically by barium, that existing as sodium sulphate is subtracted, and the remainder calculated as sulphur.

(f.) A known weight is treated with hydrochloric acid, the filtrate oxidised by nitric acid, and the mixed iron, alumina, and phosphoric acid precipitated by ammonia.

(g.) The filtrate from (f) is treated with ammonium oxalate, the precipitate estimated volumetrically by permanganate, or gravimetrically as calcium oxalate; hence the calcium may be known.

(h.) A known weight is lixiviated with warm water, and in the filtrate from the insoluble matter the silica is estimated by evaporation to dryness with hydrochloric acid; in the filtrate from this the aluminium combined as aluminate is determined by precipitating the alumina by ammonia.

(i.) A known weight is cautiously treated with sulphuric acid in a capacious platinum crucible, and heated till gases cease to be evolved; the residue is treated with water, filtered, and well washed; ammonia and ammonium oxalate are added to the filtrate; and, ultimately, the total sodium contained weighed as sodium sulphate.

In calculating results from the foregoing data, the chlorine found is calculated as sodium chloride, the sulphuric acid as sodium sulphate, the silica as sodium silicate, and the aluminium (soluble in water) as sodium aluminate; the remaining sodium is then calculated as sodium carbonate, and the remaining carbonic acid as calcium carbonate. The sulphur is calculated as calcium sulphide, and the remaining calcium as lime. From the total alumina, iron, and phosphoric acid the alumina present as aluminate is subtracted; the coke and sand, &c., are directly determined (a). The difference from 100 in a carefully

conducted analysis will not amount to more than a few tenths per cent., and represents cyanogen, traces of moisture, &c., and loss.

In an over-roasted ash the alkaline sulphide can only be safely estimated by digestion with nearly absolute alcohol, oxidation to sulphate by chlorine, and precipitation by barium chloride. The sodium contained as poly- or mono-sulphide, may be determined volumetrically by test acid in the alcoholic solution, and must be subtracted from that to be calculated as sodium carbonate as above; the sulphur existing as sodium poly- or mono-sulphide must be subtracted from the total sulphur found, the difference being calculated as calcium sulphide.

Soda-Ash.—The commercial valuation of soda-ash is usually restricted to the determination of the percentage of 'available alkali' contained therein, by this term being meant the total sodium oxide (anhydrous) contained in a state capable of saturating a strong acid, as sulphuric; and hence including hydrate, carbonate, aluminate, silicate, sulphide, sulphite, and thiosulphate. The analysis is usually performed by adding the standard acid to the hot aqueous solution of a known weight of ash, until a slight acid reaction is obtained; by this means all the lime and the alumina contained as aluminate are estimated as though they were soda. Practically this error is of slight importance; it may be readily avoided by addition of a very slight excess of acid along with some tincture of litmus, then adding a slight excess of standard sodium carbonate solution, boiling and filtering from the precipitated lake and calcium carbonate; the excess of sodium added is now again determined by the standard acid, and thus the exact amount of acid used to saturate the sodium oxide present in the 'available' state is known.

Mr. Pattinson, of Newcastle-on-Tyne, has lately drawn public attention to a strange error made by some analysts in attempting to apply the English commercial test for soda to samples of alkali, soda-ash, &c., the result of which error is to make the test indicate from 1 to $1\frac{1}{2}$ per cent. more soda than the sample contains by the proper English test. It is well known that the English soda-test had its origin in the early days of the soda trade—when chemists believed the equivalent of soda to be 32, and that of sodium carbonate 54; and consequently, test acid was made so that 40 parts of sulphuric acid neutralised 54 parts of sodium carbonate, equal to 32 of soda. This method of testing has always been, and still is, used by the soda trade throughout England; and it is a custom well understood by both buyers and sellers. It indicates 0.66 per cent. more soda in a 50 per cent. alkali than the rigidly-correct test based on the new equivalent 31 would indicate. It is certainly desirable, for the sake of scientific accuracy, that the correct equivalent, 31, should be used in testing; but, seeing that manufacturers have expended their capital in plant, and made their contracts for their various materials on the under-

standing that a product containing a certain percentage of soda would be obtained, and seeing that there are other commercial customs of the trade still in force, which tell as much against the manufacturer as the test does in his favour—such, for instance, as that of not charging for fractions of percentages—it is more the province of an association like the Alkali Manufacturers' Association than that of an analytical chemist to make alterations in trade usages affecting such vast interests. Certainly, if any alteration be made at all by chemists, it should be made in the direction of scientific accuracy, and not in the contrary direction, as in the case above referred to. The error arises in this way: the test acid is made so as to indicate the exact amount of soda according to the new and correct equivalent 81—that is, that 40 parts of sulphuric acid should neutralise 53 parts of sodium carbonate, equal to 81 parts of soda.

To convert the results obtained by this test acid into the English commercial soda-test, it is incorrectly assumed that the 81 parts of soda are equal to 82—in other words, that the 53 parts of sodium carbonate contain 82 parts of soda. This is where the error lies: for, according to the correct English test, 54 parts of sodium carbonate, and not 53, contain 82 of soda; and, therefore, by the English test, 53 parts of sodium carbonate contain only 81.41 of soda. By thus mixing up the old and the new systems of equivalents, a sample of soda-ash which, by the correct English test, contains 50.66 per cent., would be returned as containing 51.61 per cent. of soda. A sample of caustic soda which, by the correct English test, would contain 75.0 per cent. of soda would, by this erroneous method, indicate 76.4 per cent. It is only necessary to point out this error in order that it may be avoided and guarded against by anyone interested in the buying and selling of alkalis.

When the exact composition of a sample of soda-ash is required, the following method may be adopted:

(a.) A known weight is heated to 150°—200° C., and the loss of weight considered to be moisture.

(b.) The residue of (a) treated with hydrochloric acid leaves sand and insoluble matter, and in the filtrate the sulphuric acid may be estimated volumetrically, or, better, gravimetrically by barium chloride.

(c.) The carbonic acid present is estimated in Mohr's apparatus, or in Fresenius and Will's, with the addition of some potassium chromate.

(d.) A known weight is treated with water, and the solution evaporated to dryness with hydrochloric acid; thus the silica is determined: in the filtrate from this ammonia throws down alumina, from which the aluminium, as aluminate, is known.

(e.) The insoluble residue of (d) with hydrochloric acid and ammonia gives the iron and alumina (not as aluminate); the filtrate from this with ammonium oxalate gives the calcium (usually only traces).

(f.) A known weight is dissolved in nitric acid, and the chlorine estimated by a standard silver solution.

(g.) A known weight dissolved in water is oxidised by chlorine, and the sulphate thus formed determined; another known weight is dissolved in water and the solution divided into two equal parts; in one the iodine required to yield a blue colour when starch and acetic acid are added, is determined, to the other zinc sulphate is added, and in the filtrate the iodine required after removal of the precipitated zinc sulphide is again determined; from these data the sulphide, sulphite, and thiosulphate are calculable.

(h.) The total 'available alkali' is determined, the error due to the aluminium of the aluminate being eliminated as previously mentioned; subtracting from this, calculated as sodium, the sodium corresponding to the silica, alumina, sulphide, sulphite, thiosulphate, and carbonic acid found, the difference is calculated as hydrate; this may be checked by adding barium chloride to a known weight, and determining the amount of acid required to neutralise the filtrate: rather more hydrate is usually indicated by this mode than what is really present, owing to the presence of a portion of aluminate, thiosulphate, &c., incompletely thrown down by the barium salt.

Carefully executed analyses according to this method have yielded results adding up to between 99.8 and 100.1.

When ferrocyanide is present, it may be estimated by dissolving a known weight of ash in hydrochloric acid, and adding iron perchloride; after standing some time, the precipitated Prussian blue may be well washed, treated with pure potash, and the ferrocyanide determined in the solution by permanganate.

M. Jean has proposed a somewhat different method of analysing soda-ash and caustic soda. His process, which, although it does not give quite so accurate results as those already described, may occasionally be found useful, is as follows: Take 4 grammes of the sample to be analysed, and dry completely at from 110° to 120° C.; the difference between the weight of the quantity originally taken and the weight after drying gives the quantity of water. Take 1 gramme of this dried material, place it in a glass tube, and pass a current of dry carbonic acid gas over the substance for about an hour; dry it again at 110°, to drive off any mechanically-adhering carbonic acid; place the substance upon a filter, and exhaust with tepid water, until the wash water is no longer precipitated by barium chloride.

The filtrate is collected in a glass flask with flat bottom, and barium chloride is added to it. The liquid is left to settle, and, on having become quite clear, is drawn off from the precipitate by means of a pipette, and the precipitate of barium carbonate is collected on a tared filter, washed with boiling water, dried, and weighed. If there happen to be sulphates present, the sulphuric acid is precipitated, along with the barium carbonate, as barium sulphate; and the weighed barium

carbonate is, therefore, washed with water acidulated with hydrochloric acid, again washed with warm water, and, after drying, weighed.

In order to estimate the sodium carbonate, 1 gramme of the dried sample is taken, dissolved in water, precipitated with barium chloride; the precipitate is collected on a tared filter, and after having been washed and dried, the weight of the barium sulphate is deducted from the weight found. The difference of the weights of the barium carbonates found by these two operations indicates the quantity of barium carbonate which, by calculation, has to be converted into caustic soda; the second assay gives the quantity of sodium carbonate. In order to estimate the sodium sulphide contained, 1 gramme of the dried material is again taken; this quantity is dissolved in water, and estimated according to the following process.

Estimation of Soluble Sulphides in Commercial Soda and Soda-Ash.—These may be readily estimated by the following method, based on the insolubility of silver sulphide, and the solubility of all the other argentiferous salts, in presence of ammonia. The process was originally devised by H. Lestelle.

Prepare a normal solution of ammoniacal silver nitrate by dissolving 27.69 grammes of fine silver in pure nitric acid, adding 250 c.c. of ammonia, and diluting with water to bring the volume to 1 litre. Each c.c. of this solution corresponds to 0.01 gramme of sodium monosulphide.

Dissolve the substance to be analysed in water, add ammonia, boil, and then add, drop by drop, by means of a burette divided into tenths of a c.c., the ammoniacal silver solution, and a black precipitate of silver sulphide takes place. When nearly all the sulphur is precipitated, filter, and into the filtered liquid pour a fresh quantity of silver solution, until, after repeated filtrations, a drop of this liquid produces only a slight opacity. The estimation is then at an end, and it is only necessary to read the divisions indicated by the burette, and to convert this number into the corresponding amount of sodium sulphide.

To estimate very small quantities of sulphide, the argentiferous liquid must be more diluted, so that each c.c. corresponds to 0.005 gramme of sulphide. The presence of chloride, sulphate, and sodium carbonate, caustic soda, &c., makes no difference in the accuracy of this method, by reason of the solubility in ammonia of the precipitates given by these bodies with silver nitrate.

Analysis of Mixtures of Alkaline Mono- and Bi-carbonates.

A. Mebus.—Two equal portions of the mixture are weighed out, and in one of them the total alkali is determined by means of a standard acid. Into the solution of the other portion is poured a standard solution of caustic soda, perfectly free from carbonic acid, and corresponding in quantity with the alkali just found to be present, i.e. as many equivalents of alkali are added as are already contained. Of the alkali thus added, one portion combines with half the carbonic acid of

the bicarbonate, and the remainder, which is precisely equal in quantity or equivalent (according as the base added is identical with or different from the base of the salts under examination) to the alkali of the monocarbonate, remains in a free state in the liquid. This solution is then precipitated with an excess of barium chloride, the carbonates are thus eliminated as barium carbonate, and after filtration there remains in the filtrate merely the excess of barium chloride, sodium chloride, and a quantity of free caustic soda equivalent to the alkali of the monocarbonate. All that remains is to take a known fraction of this liquid, and determine the alkali in the usual manner. We have thus the alkali of the monocarbonate, and by subtracting it from the total alkali we find the alkali of the bicarbonate.

Separation of Potassium from Sodium.

To separate potassium from sodium when in presence of sulphuric acid, Finkener proposes the following:—Add hydrochloric acid to the aqueous solution to be analysed; then solution of platinum chloride until the liquid is deep yellow. Add water sufficient, when boiling, to dissolve the double salt precipitated; evaporate to syrupy consistence, but do not dry; extract, and wash on a filter with a mixture of alcohol (specific gravity 0.8) 2 volumes, ether 1 volume. Wash well with solution of ammonium chloride; this decomposes the sodium sulphate and allows it to be washed away. The filtrate, alcoholic extract, and washings contain the sodium. Heat the filter and its contents in a stream of hydrogen—a temperature of 240° suffices; extract the potassium chloride with water, and weigh, or titrate with silver solution.

A great excess of sulphuric acid is to be avoided. The ammonium chloride solution dissolves about 0.18 to 0.26 per cent. of the potassium platino-chloride, but the quantity so lost varies with the strength of the solution, its temperature, and the quantity of free hydrochloric acid in it. On the other hand, the double salt carries down with it about 0.16—or 0.85 per cent. of sodium salt.

Under ordinary circumstances these metals may best be separated by the method given in pp. 1, 2, &c.

Indirect Estimation of Potassium and Sodium.

The direct method of estimating potassium and sodium—viz. by the precipitation of the former as potassium platino-chloride, and reckoning sodium from the loss—though sufficiently accurate in patient and skilful hands, is yet open to many sources of error, and at the best is exceedingly tedious and troublesome.

The indirect method does not appear to possess the confidence of chemists—at least, it is rarely mentioned in published investigations. Mr. P. Collier, B.A., Assistant in the Sheffield Laboratory, Yale College, U.S.A., has published (*Am. Journ. Sci.* xxxvii. 944) a number of experiments to ascertain the limits of error in this process.

The volumetric estimation of chlorine as perfected by Mohr offers by far the best basis for an indirect determination of the alkalis. It is, in fact, requisite, in employing the usual direct method, to procure the alkalis in the condition of pure chlorides before precipitation.

When the alkaline chlorides are obtained free from all foreign matters, it is but the work of a few moments to ascertain their contents of chlorine.

The silver solution used for this purpose is best prepared by weighing off in a porcelain crucible about 4.8 grammes of clear crystallised silver nitrate, fusing it at the lowest possible heat, and then ascertaining its weight accurately. After fusion it should weigh a little more than 4.7988 grammes, the quantity that, contained in a litre of water, gives a solution of which 1 c.c. = 0.001 gramme of chlorine. The fused salt is dissolved in a little warm water, the solution brought into a litre flask and filled to the mark, observing the usual precautions as to temperature, &c. When thus adjusted, add to the contents of the flask, from a burette, enough water to bring the excess of silver nitrate above 4.7988 grammes to the requisite dilution. In this way it is easy, with a burette and litre flask, to make a perfectly accurate standard solution, while this would be hardly possible should the operator weigh off less than 4.7988 grammes of silver nitrate.

This solution, which may be preserved in a well-stoppered bottle indefinitely, without change, is next tested by means of a solution of pure sodium chloride or ammonium chloride; a quantity, say about 2 grains, of one of these salts being dissolved in a litre of water and 10 c.c. of the liquid taken for the comparison. The solution being ready, the estimation of chlorine is conducted as described by Mohr, Fresenius, Sutton, and others, potassium chromate being employed to indicate the completion of the reaction. The use of Erdmann's float in a burette (which may hold 70 c.c.) graduated to fifths ensures the needful accuracy of reading. Two-tenths c.c. of silver solution may be deducted as the excess needed to produce a visible quantity of silver chromate.

From a long list of analyses given by the author, it is shown that the indirect method is in all cases equal in accuracy to the ordinary separation, while in the matter of convenience and economy of time there is no comparison between them. In no case does the difference between the quantities taken and found of either alkaline chloride exceed two milligrammes, and in most instances it is less than one milligramme. The correspondence between the amounts of chlorine as taken and found is, of course, still more near. The error that appears in the estimation of the chlorides would be considerably reduced, if, as usually happens, the metals were calculated as oxides.

The following are the formulæ employed for calculating the quantities of NaCl and KCl, or of Na₂O and K₂O, contained in or

corresponding to any mixture of alkaline chlorides whose total weight and amount of chlorine are known :—

W = weight of mixed chloride

C = weight of chlorine

$$\text{NaCl} = C \times 7.6811 - W \times 8.6288$$

$$\text{KCl} = W \times 4.6288 - C \times 7.6811$$

$$\text{Na}_2\text{O} = C \times 4.0466 - W \times 1.9248$$

$$\text{K}_2\text{O} = W \times 2.9248 - C \times 4.8210$$

Rapid Estimation of Potassium and Sodium.

M. Jean grinds up the saline mixture, in which it is desired to determine the potash and soda, with an excess of ammonium sulphate, moistened with a few drops of water, heated to redness in a platinum crucible till the ammoniacal salts have completely disappeared, and heated once more with ammonium sulphate in the same manner, so as to ensure the expulsion of all acids capable of displacement by sulphuric acid. The substance is then dissolved in boiling water, a slight excess of baryta-water is added, and the sulphates and insoluble matters are removed by filtration. The filtrate is then treated with a little seltzer-water, and kept at a boil till all excess of carbonic acid has been expelled, and all the barium carbonate rendered insoluble. The solution is then filtered, when the potash and soda remain in the filtrate in the state of carbonates, and are exactly neutralised with a standard solution of hydrochloric acid at the boiling-point. In this neutral liquid the weight of the chlorides present is determined by bringing the solution—by evaporation or by the addition of water, as the case may be—to a volume of 50 or 100 c.c., the specific gravity of which is then determined; or the solution may be evaporated to dryness, and the residue may be weighed. Knowing, therefore, from the quantity of hydrochloric acid used in filtration, the weight of chlorine corresponding to the two alkalies and the weight of the two chlorides, it is easy to calculate the proportions of potash and soda. If the chlorine found is multiplied by 2.1029, the weight of the chlorides subtracted from the product, and the remainder multiplied by 3.6288, we obtain the weight of sodium chloride, whilst the difference will be the potassium chloride. If it is required to determine alkalies in presence of a superphosphate, it is prudent to neutralise with baryta-water before adding ammonium sulphate to prevent the formation of pyrophosphates.

M. F. Maxwell Lyte proposes the following indirect method for determining potash and soda :—Having obtained the mixed sulphates free from any other salts, and in solution, evaporate the mixture to dryness, heat to redness and weigh. Now redissolve the salts, and estimate the *percentage* of sulphuric anhydride they contain by any convenient volumetric or gravimetric method, and from the *percentage* thus found subtract the *percentage* of sulphuric anhydride the salt

would contain were it pure potassium sulphate. The figures 45·977 are a sufficiently close approximation to this last-named percentage, and by simply multiplying the remainder by 9·66, the result will be the percentage of sodium sulphate the mixed salts contained.

This result is not absolutely correct, for the multiplier is a little too high, but the error is not $\frac{1}{1000}$, which is near enough for all practical purposes.

The result obtained deducted from 100, the remainder will be the percentage of potassium sulphate, and from these results the quantities of each of the alkalis sought may be calculated.

Estimation of Potash and Soda in Minerals.

W. Knop and J. Hazard dissolve in hydrofluoric acid, evaporate, drench the residue with concentrated sulphuric acid, thus removing the bulk of the silicon fluoride. The sulphuric acid is then evaporated off, the dry residue moistened with five or six drops of concentrated sulphuric acid, heated, drenched with 150 c.c. water, and barium hydrate added till red litmus-paper is turned distinctly blue. The mixture of barium sulphate, silica, alumina, magnesia, and ferric oxide is then filtered off and well washed. The filtrate is evaporated to dryness, adding, when it is concentrated down to about 200 c.c., a few grammes of dry ammonium sesquicarbonate. When perfectly dry the residue of barium and calcium carbonate is extracted successively fifteen times, each time with 20 c.c. water, the liquid being each time filtered through a small filter of 8 to 4 c.m. diameter into a platinum capsule, and evaporated to dryness. The residue is drenched again with 20 c.c. water, the water is decanted through a similar fresh filter, and the solution, after it has deposited a little barium carbonate with some alumina and iron, is collected along with the washings in a fresh platinum capsule. The alkaline carbonate, to which a few more granules of ammonium carbonate have been added, is again dissolved in 20 c.c. water, observing that no residue remains. The liquid is then neutralised with hydrochloric acid, evaporated, the chlorides dried strongly, and the potassium and sodium separated by means of platinum chloride.

LITHIUM, CÆSIUM, AND RUBIDIUM.

Lithium, Cæsium, and Rubidium, Extraction of from Lepidolite.

The following process has been found to answer well on a large scale:—Fuse the mineral at a red heat, pour it into cold water, pulverise and wash it, and treat the washed mass with twice its weight of hydrochloric acid. After several hours' boiling, separate the greater part of the silica, add nitric acid to peroxidise the iron, and precipitate by sodium carbonate, the solution being made so weak that the

lithium carbonate will not be thrown down. After evaporation in this way in an iron vessel, to separate more magnesium carbonate, saturate with hydrochloric acid and add the proper quantity of potassium platino-chloride to precipitate all the rubidium and caesium. The filtered liquid, containing an excess of platinum and lithium, is treated with sulphuretted hydrogen to separate the platinum, then concentrated and mixed with sodium carbonate to precipitate the lithium carbonate. By this method 1000 parts of lepidolite will give 78 parts of lithium carbonate, 6.5 parts of rubidium and caesium chlorides, supposing the operation to be continuous. The advantage of this process consists in the direct fusion of the mineral, and it may be applied to all lithian micas. If thallium is present, which is frequently the case, it will be precipitated as thallium platino-chloride along with the rubidium and caesium.

Estimation of Lithia by Sodium Phosphate.

Berzelius detected lithia in Carlsbad water by evaporating the solution of the alkalis with phosphoric acid and sodium carbonate. On treating the whole with water, an insoluble sodium and lithium phosphate remained. This double salt has been shown by C. Rammelsberg to be a variable mixture of the two phosphates. Mayer, however, contradicted these results and denied the existence of a double phosphate, and contended that the above residue was pure lithium phosphate. C. Rammelsberg has repeated his former experiments and completely confirmed them, preparing synthetically double salts having sodium to lithium as 1 to 8, or 9 to 2, and therefore he concludes that lithium cannot be determined by Mayer's method, which is also recommended by Fresenius. The employment of this process for the estimation of lithium in micas has led to too high a percentage of lithium. Lithium and sodium chlorides may be separated by treatment with ether and alcohol.

Cæsium and Rubidium, Extraction of from Mineral Waters.

Compounds of these rarer alkali metals may be separated in the following manner from saline mother liquors derived from the evaporation of some mineral waters. A boiling dilute solution of platinum chloride added to a boiling, rather dilute solution, containing potassium, rubidium, and caesium, will precipitate the latter metals with but a very small proportion of the first. The platinum being removed from this precipitate by means of sulphuretted hydrogen, the alkaline metals are again brought into dilute solution as chlorides; the solution is heated to boiling, and once more a dilute solution of platinum chloride is added in two portions. After each addition the liquor is filtered, while boiling, through a water-bath filter, and the precipitate is washed in hot water; the solution is then allowed to cool and deposit. In this way three precipitates are obtained; the first contains

nearly all the cæsium, the second almost all the rubidium, and the third, deposited on cooling, is, for the most part, the potassium compound. By repeating these precipitations the compounds may be almost completely separated. The cæsium and rubidium may be finally separated from each other by one of the methods subsequently described (page 27).

Cæsium and Rubidium, Extraction of from Lepidolite.

Dr. Oscar D. Allen, of Yale College, has shown that the lepidolite occurring at Hebron, in Maine, U.S., contains these metals in comparative abundance, and he has recommended the following process for their extraction from this mineral. The process used is based upon that employed by Professor J. Lawrence Smith, for the determination of alkalis in silicates (for this process, see page 28). Ten parts of the pulverised lepidolite are first mixed with 40 parts of coarsely-powdered quicklime; a mixture of enough water to slake the quicklime, with hydrochloric acid sufficient to form from 6 to 7 parts of calcium chloride is next made ready; the two mixtures are then united and stirred vigorously during the process of slaking, thus intimately blending the mineral with suitable proportions of dry hydrate of lime and calcium chloride. Practically as good results are obtained when the lepidolite is powdered sufficiently fine to pass through a sieve of twenty holes to the linear inch, as when it is more finely pulverised; the fact being that the foliated structure of the mineral exposes a large surface to the decomposing agency of the lime mixture.

This mixture is heated to redness for six or eight hours, in Hessian crucibles. Care must be taken to avoid a heat much above redness, as otherwise alkaline chlorides volatilise in dense clouds, and the mass fusing is absorbed to a considerable extent into the crucible and lost.

The agglomerated product obtained from the ignition of this mixture is detached from the crucible, and boiled with water from a quarter to half an hour, and washed till all but a trace of the chlorides is removed. The solution thus procured, containing calcium chloride and the chlorides of the alkali metals, is evaporated till crystals begin to form; then sulphuric acid is added as long as calcium sulphate separates, taking care to avoid excess; and the whole mass is evaporated to dryness and strongly heated to expel free hydrochloric acid. The residue is treated with water, and the small quantity of calcium sulphate which goes into solution is precipitated with ammonium carbonate. The filtered solution is again evaporated to dryness and ignited.

In this manner is obtained a mixture of salts, consisting of the chlorides with a small admixture of sodium, potassium, lithium, rubidium, and cæsium sulphates. By treating this by the process of fractional precipitation with platinic chloride, a mixture of the cæsium

and rubidium platino-chlorides is obtained, in which no potassium can be detected with the spectroscope. The platinum salts are to be gently heated in a current of hydrogen, until a complete reduction of the platinum takes place, when the alkaline chlorides may be extracted with water.

By working in the above manner Dr. Allen obtained from 10½ kilogrammes of lepidolite 2169 grammes of crude alkaline chlorides, which yielded 172 grammes of mixed caesium and rubidium platino-chlorides, equivalent to a yield of about $\frac{1}{2}$ per cent. of the two metals from the lepidolite.

In separating the caesium and rubidium platinum salts from that of potassium, a not inconsiderable amount of these metals goes into solution with the potassium salt, thus materially diminishing the quantity obtained; much the larger proportion of this loss is rubidium, due to the greater solubility of its platinum salt. This can in great measure be recovered by a repetition of the treatment.

Separation of Potassium, Sodium, and Lithium.

If potassium, sodium, and lithium are present in the same solution, first separate lithium as phosphate, and then proceed as in the separation of potassium and sodium; or convert the three into platino-chlorides, extract the sodium and lithium salts with a mixture of alcohol and ether containing a little hydrochloric acid, and wash with a mixture of absolute alcohol 6 volumes, ether 1 volume; the residue is pure potassium platino-chloride. Direct experiments show that the above method is not vitiated in any degree by the presence of hydrochloric, nitric, phosphoric, arsenic, or boric acids, or salts of magnesium, zinc, manganese, iron, aluminium, nickel, or copper.

Antimony Chloride as Reagent for the Caesium Salts.

If the solution of caesium salt, not too dilute, is mixed with a solution of antimony chloride in concentrated hydrochloric acid, a white crystalline precipitate is at once formed which, according to R. Godefroy, does not disappear on the addition of hydrochloric acid. The solutions of the other alkali metals yield no precipitate if similarly treated. The precipitate may be filtered, washed with concentrated hydrochloric acid, and redissolved in the same acid much diluted. The solution yields on evaporation well-developed, hard, permanent crystals belonging to the hexagonal system. They may be obtained pure by repeated solution in dilute hydrochloric acid, and recrystallisation. They contain 88.419 per cent. of chlorine, and of antimony 80.581 per cent., corresponding to the formula $\text{SbCl}_3 \cdot \text{CsCl}$. This salt is decomposed on the application of heat, and on treatment with water. It is completely soluble in dilute acids. Charples and Stolba observed a similar reaction of the caesium salts with stannic chloride. The rubidium salts, however, give with tin chloride a precipitate which is

very sparingly soluble. The presence of ammonia in the liquid contaminates the double caesium and tin chloride with pink salt. The reaction with antimony chloride is not interfered with either by ammonia or rubidium. The liquid must be strongly acid to prevent the precipitation of antimony oxychloride.

Separation of Cæsium from Rubidium.

The plan recommended by Dr. Allen for separating these metals depends upon the fact that bitartrate of rubidium requires about eight times as much water for its solution as the caesium bitartrate, and hence they are easily separated by crystallisation.

The mixed chlorides are converted into carbonates by first converting them into sulphates, separating the sulphuric acid by caustic baryta, and removing the excess of baryta by carbonic acid. To the alkaline solution thus obtained twice as much tartaric acid is added as is necessary to neutralise it. This solution is concentrated until it is nearly saturated at 100° C. The crystals, which deposit on cooling, show the rubidium lines more intensely than did the original mixture, whilst the caesium lines are much fainter. This product is dissolved and recrystallised from hot saturated solutions three times. The caesium reaction in these successive crops diminishes until, in the fourth, it disappears, leaving the rubidium spectrum in entire purity.

The solution from which the first crystals have been removed is concentrated to nearly one-half its original volume, when, on cooling, a very small quantity of salts of the two alkalies is deposited. On repeating this operation three times, a portion of the solution, evaporated to dryness and examined by the spectroscope, gives only the lines belonging to caesium. The several intermediate products containing both alkalies are then united, and another portion of each salt is separated from them in the same manner. By repeating this process of fractional crystallisation four times, about 90 per cent. of a mixture of these alkalies may be separated in a perfectly pure state. It requires no great expenditure of time, since the solutions employed can be concentrated at high temperatures, and, on cooling, immediately deposit well-formed crystals.

Bunsen's recent method for the separation of caesium and rubidium is somewhat similar to the above, but it has the advantage that it can be effected when working on a much less bulk of material. It is as follows:—In a mixture of pure caesium and rubidium chlorides the chlorine is determined, and from its amount that of rubidium is calculated. The chlorides are converted into carbonates, and to the latter salts a little more tartaric acid is added than is necessary to produce neutral caesium tartrate and rubidium bitartrate. The mixture, dried and pulverised, is brought upon a funnel, whose neck is stopped by a small filter, and the whole is placed in an atmosphere saturated

with moisture. The neutral caesium salt deliquesces, and passes the filter, while the acid rubidium salt remains behind.

Separation of the Alkalies from Silicates not Soluble in Acids.

One of the best processes for separating the alkalies from silicates is the one devised by Professor J. Lawrence Smith, M.D. It is sufficiently accurate to be available for their quantitative estimation. This process has scarcely received the attention it deserves, and as it appears to be almost unknown in England, it is considered advisable to give the description mainly in Dr. Smith's own words rather than in a condensed abstract.

1. 'In this description of separating and determining the alkalies, it is my intention to give the minutest details, although it may be thought useless by some; but numerous analyses have given me the experience here detailed; and I am convinced that analytical chemists, if they follow them out, will never resort to any other known method after a few trials; and if there be a better method, it is yet to be discovered. The presence of boracic, hydrofluoric, and phosphoric acids in the minerals in no way interferes with the process. Even in silicates *soluble in acids*, I prefer this method, in common with other analysts, for its ease and accuracy.

2. 'During the latter part of 1852 I made the researches, the details of which were published early in 1853.¹ Since that time I have employed the process many hundreds of times with the greatest satisfaction, most accurate results, and ready manipulation; some minor points were not completed satisfactorily until several years after the first notice of the method; these have been subsequently perfected, and in my mind there is nothing further now to be desired. I might state that many analytical chemists have for years constantly used this process to the exclusion of all others.

3. 'The purpose of this article is to give all the perfections, and a minute detail of the manipulations, with whatever precautions are necessary, all of which are simple and easily executed. In the two articles on the subject of alkali determination in minerals, published in 1853, the whole subject was reviewed, which it is needless to recur to now. I then reviewed the process by caustic baryta and its salts, by hydrofluoric acid, also detailing some experiments on the separation of the different alkalies from each other, microscopic examinations of the same, &c. It was shown that after the caustic alkalies, the most powerful agent to attack silicates at a high temperature is caustic lime, a fact not new to chemists, for as early as 1847 I used this process for attacking silicates, and others had done the same prior to that period.

¹ 'Shortly after my first publication, M. St. Claire Deville made known his method of analysing the silicates by *fusion* with lime; but the nature of his process and the objects to be arrived at were quite different from those attained by the process under consideration.

But for the purpose of arriving conveniently at a *quantitative determination of the alkalies in silicates*, certain methods of manipulation, quantity of material, admixture, &c., had to be discovered, and in them resides the success of my process—converting the most difficult parts of the analysis of a silicate into the easiest.

4. 'The methods of analysis of the silicates by caustic baryta and its carbonate are well known; but for various reasons fully detailed by Rose, in his "Analytical Chemistry," are now no longer used. The method still employed extensively is the one proposed by Berzelius, with hydrofluoric acid, and when applied with numerous precautions, it seems to decompose all silicates; still, according to Rose, there are siliceous compounds that cannot be completely decomposed by hydrofluoric acid.¹ Dismissing all criticism, I at once proceed to the method which is the subject of this article.

5. '**Decomposition of Silicates by Ignition with Calcium Carbonate and Sal-Ammoniac.**—This mixture of calcium carbonate and sal-ammoniac is used simply for the purpose of bringing in a most thorough manner caustic lime to act upon the silicates at a red heat.² The first step in the process is to have pure *carbonate of lime*.

6. 'This is made in my laboratory as follows:—Take as good marble as can be conveniently found (not dolomitic), or calc spar, and dissolve in hydrochloric acid. (It is not necessary that the acid be perfectly pure). Add an excess of the marble and warm the solution: to it add lime-water or some milk of lime, made from pure or nearly pure lime, until the solution is alkaline to test-paper; the lime is added to precipitate any magnesia, phosphate of lime, &c., that may have been in the marble. Filter this solution, and after heating it to at least 160° F., precipitate with ammonium carbonate.³ The calcium carbonate thus precipitated is to be thrown on a filter and well washed with pure rain-water or with distilled-water.

7. 'Thus prepared, the calcium carbonate is a dense powder and perfectly pure; or, if it contain any impurity, it will be a trace of barium or strontium carbonate which in no way interferes with the use of the calcium carbonate.

¹ 'The process used by Deville in fusing with lime is in most cases better than that by hydrofluoric acid, and one that I should use in preference to all others, except the one now being described.

² 'Calcium chloride at a red heat will dissolve more or less caustic lime.

³ 'This precaution must not be overlooked, as it is desirable to obtain the precipitated calcium carbonate as dense as possible. If the ammonium carbonate be added to the cold solution, the precipitate, at first gelatinous, will ultimately become much more dense and settle readily; the same is true if the mixture be heated after the addition of the ammonium carbonate; but in neither case will it be as dense as when the carbonate is added to the hot solution of calcium chloride. The reaction in this process of analysis is in no way affected by the form of the calcium carbonate; but by using the denser form, the mixture occupies less space in the crucible in which it is heated.

8. '**Sal-Ammoniac.**—To give to this reagent the most convenient form, take fragments of clean sublimed sal-ammoniac, dissolve them in water over a gentle fire, filter, evaporate the filtered solution over a steam-bath, or on a sand-bath, or any other convenient gentle heat, and as the small crystals deposit themselves, stir the solution to keep the crystals small; when one-half or two-thirds of the sal-ammoniac is deposited, pour off the liquid without waiting for it to cool, throw on a cotton filter, and dry the crystals at the temperature of the atmosphere. In this way, sal-ammoniac is furnished that is easily pulverised.

9. '**Vessels for Producing the Decomposition.**—The ordinary platinum crucible can be employed for this purpose, and is now most commonly used, and for many years was used by myself. It is, however, found that, while this method exceeds in precision and ease all other known methods for alkali determinations in silicates, there was yet a very minute quantity of alkalis lost by volatilisation, and while the method gave satisfaction to those who used it, I yet continued my researches to overcome even this small loss. This has been successfully accomplished, and for some time I have been in the constant habit of using an improved form. Instead of the ordinary platinum crucible, I use an elongated one, which may be made of various dimensions. The one employed, with from $\frac{1}{2}$ to 1 gramme of silicate, is of the following form and dimensions.

10. 'An elongated slightly conical crucible with rounded bottom, and having a cover with or without a central wire to hold the cover; its length is 95 millimetres; diameter of opening 22 millimetres; diameter of small end, just at the turn of the bottom, 16 millimetres; and weighs about 85 or 40 grammes. It can be made lighter, but experience has shown that it is better if stiff and solid. Messrs. Johnson and Matthey, Hatton Garden, London, have made a number for me, and they have my drawings and directions. It is thus made for the purpose of having that portion of the crucible containing the mixture heated strongly, while the upper portion is below a red heat.

11. '**Manner of Heating the Crucible.**—If the ordinary crucible be used, it is heated in the manner usually employed for the fusion of silicates. If the new form of crucible be employed, then the upper part may be grasped by a convenient metallic clamp in a slightly inclined position, and a moderate blast from the table blowpipe made to play upon it for about 25 or 30 minutes. But now gas is to be found in every well-mounted laboratory, Bunsen burners of all dimensions are used, and when properly applied, can be made to give gradations of heat, from the mildest to that sufficient to melt cast-iron. A simple, cheap, and convenient furnace, with a properly-arranged draught, can be made to accomplish all silicate fusions without the aid of any manual labour, and therefore I employ such an apparatus, of which a description will be given at the end of this article.

12. 'Method of Analysis.—We have now the pure calcium carbonate, granular sal-ammoniac, and the proper crucible. The silicate is to be well pulverised in an agate mortar;¹ for the analysis I take $\frac{1}{2}$ or 1 gramme, the former is most commonly used, as being sufficient, and best manipulated in the crucible used; a gramme, however, may be conveniently employed. The weighed mineral is placed in a large agate mortar, or better in a glazed porcelain mortar of $\frac{1}{2}$ to 1 pint capacity. Weigh out an equal quantity of the granular sal-ammoniac (a centigramme more or less is of no consequence), put it in the mortar with the mineral, rub the two together intimately; after which add 8 parts of calcium carbonate in three or four portions, and mix intimately after each addition; empty the contents of the mortar completely upon a piece of glazed paper, that ought always to be under the mortar, and introduce into the crucible. The crucible is tapped gently upon the table and the contents settled down.

13. 'It is then clasped by a metallic clamp in an inclined position or it is placed in the support referred to in the latter part of this article, leaving outside about $\frac{1}{2}$ or $\frac{3}{4}$ inch; a small Bunsen burner is now placed beneath the crucible, and the heat brought to bear just about the top of the mixture, and gradually carried toward the lower part, until the sal-ammoniac is completely decomposed, which takes about 4 or 5 minutes; heat is then applied in the manner suggested, either with the blast or with the burners referred to, acting by its own draught, and the whole kept up to a bright red heat, for about from 40 to 60 minutes. It is well to avoid too intense a heat, as it may vitrify the mass too much.

14. 'The crucible is now allowed to cool, and, when cold, the contents will be found to be more or less agglomerated in the form of a semi-fused mass; a glass rod or blunt steel point will most commonly detach the mass, which is to be dropped into a platinum or porcelain capsule of about 150 c.c. capacity and 60 or 80 c.c. of distilled water is added. In the course of a longer or shorter space of time, the mass will slake and crumble after the manner of lime; still better, this may be hastened by bringing the contents of the capsule to the boiling-point, either over a lamp or water-bath. At the same time, water is put into the crucible to slake out any small particles that may adhere to it, and subsequently this is added to that of the capsule, *washing off the cover of the crucible also*.

15. 'After the mass is completely slaked, the analysis may be proceeded with, although, as a general rule, I prefer to allow the digestion

¹ 'While in all mineral analyses, thorough pulverisation of the mineral is usually essential, still it is a singular fact that very good analyses can be made with this method, even when the powder is tolerably coarse, and in some experiments with lepidolite, powder was used with much of it in particles from $\frac{1}{16}$ to $\frac{1}{32}$ of an inch in size, giving good results. Notwithstanding this, thorough trituration of the mineral is recommended.

to continue six or eight hours, which, however, is not necessary. If the contents of the crucible are not easily detached, do not use unnecessary force, as the crucible may be injured by it, but fill the crucible to about two-thirds of its capacity with water, bring almost to the boiling-point, and lay it in the capsule, with the upper portion resting on the edge; the lime will slake in the crucible, and then may be washed thoroughly into the dish, and, as before, the cover is to be washed off.

16. 'We have now by this treatment with water the excess of lime slaked into a hydrate, and some of the lime, combined with the silica and other ingredients of the silicate, in an impalpable form; in solution there is the excess of the calcium chloride formed in the operation, and all the alkalies originally contained in the mineral as chlorides, and all that now remains to be done is to filter, separate the lime as carbonate, and we have nothing left but the chlorides of the alkalies. To do this, I proceed as follows:—

17. 'Throw the contents of the capsule on a filter (the size preferred for the quantity above specified is one 8 to 9½ inches in diameter), wash well, to do which requires about 200 c.c. of water; the washing is executed rapidly. The contents of the filter (except in those cases where the amount of the mineral is very small, and there is no more for the estimation of the other constituents) are of no use, unless it be desired to heat again, first adding a little sal-ammoniac to see if any alkali still remains in it, a precaution I find unnecessary. The filtrate contains in solution all the alkalies of the mineral, together with some calcium chloride and caustic lime; to this solution, after it has been placed in a platinum or porcelain capsule, is added a solution of pure ammonium carbonate (equal to about 1½ gramme is required).

18. 'This precipitates all the lime as carbonate; it is not, however, filtered immediately, but is evaporated over a water-bath to about 40 c.c., and to this we add again a little carbonate of ammonia and a few drops of caustic ammonia to precipitate a little lime that is redissolved by the action of the sal-ammoniac on the carbonate of lime. Filter on a small filter (2 inches), which is readily and thoroughly washed with but a little water, and the filtrate allowed to run into a small beaker glass. In this filtrate are all the alkalies as chlorides and a little sal-ammoniac; add a drop of a solution of ammonium carbonate to make sure that no lime is present. Evaporate over a water-bath in a tared platinum dish, in which the alkalies are to be weighed; the capsule used is about from 80 to 60 c.c. capacity, and during the evaporation is never filled to more than two-thirds its capacity.

19. 'After the filtrate has been evaporated over the water-bath to dryness, the bottom of the dish is dried, and on a proper support heated *very gently* by a Bunsen flame to drive off the little sal-ammoniac. It is well to cover the capsule with a piece of thin platinum

to prevent any possible loss by the spitting of the salt after the sal-ammoniac has been driven off. Gradually increasing the heat, the temperature of the dish is brought to a point a little below redness, the cover being off (the cover can be cleansed from any sal-ammoniac that may have condensed by heating it over a lamp). The capsule is again covered, and when sufficiently cool, before becoming quite cold, is placed on the balance and weighed. This weight gives as chlorides the amount of alkalies contained in the mineral.

20. ' If lithium chloride be present, it is necessary to weigh quickly, for the salt being very deliquescent attracts moisture rapidly.

' It not unfrequently occurs that the chlorides at the end of the analysis are more or less coloured with a small amount of carbon, arising from certain constituents in ammonium carbonate; the quantity is usually very minute, and in no way affects the accuracy of the analysis. In selecting pure ammonium carbonate for analytical purposes, it is well to select specimens that are not coloured by the action of the light.

21. ' It only now remains to separate the alkali by the known methods.

' **The Removal of the Sal-Ammoniac unavoidably Accumulated in the Process of Analysis.**—This is probably one of the greatest annoyances to the analyst in his examination of minerals: (1st) from the manner in which the salt creeps up the sides of the vessel in which the evaporation to dryness is carried on; and (2nd) from the great difficulty of preventing loss of the chlorides of the fixed alkalies mixed with sal-ammoniac. Owing to these difficulties, which my experience has often led me to contend with, the method about to be mentioned was contrived. It recommends itself both on account of its simplicity and certainty of operation.

' Having some time back noticed the decomposing effect produced by heating sal-ammoniac with nitric acid, the result of the investigation was that the sal-ammoniac could be completely decomposed at a low temperature into gaseous products, and it was immediately adopted in my analytical process, giving the greatest satisfaction, both as to accuracy of results as well as economy of labour.

' The manner of proceeding is as follows:—To the filtrate and washings concentrated in the way mentioned above, and still remaining in the flask, pure nitric acid is added, about 8 grammes of it to every gramme of sal-ammoniac supposed to exist in the liquid; a little experience will suffice to guide one in adding the nitric acid, as even a large excess has no effect on the accuracy of the analysis.

' The flask is now warmed very gently, and before it reaches the boiling-point of water a gaseous decomposition will take place with great rapidity. This is caused by the decomposition of the sal-ammoniac. It is no great advantage to push the decomposition with too great rapidity; a moderately warm place on the sand-bath is best

adapted for this purpose. With proper precautions the heat can be continued, and the contents of the flask evaporated to dryness in that vessel; but it is more judicious to pour the contents of the flask after the liquid has been reduced to $\frac{1}{2}$ an ounce into a porcelain capsule (always preferring the Berlin porcelain) of about $3\frac{1}{2}$ to 4 inches diameter, inverting a clean funnel of small diameter over it, and evaporating to dryness on the sand-bath or over a lamp. I prefer the latter, as at the end of the operation the heat can be increased to 400° or 500° .

' By this operation, which requires no superintendence, 100 grammes of sal-ammoniac might be separated as easily and safely as 1 gramme from 5 milligrammes of alkalis, and no loss of the latter be experienced. What remains in the capsule occupies a very small bulk; this is now dissolved in the capsule with a little water (the funnel must be washed with a little water), small quantities of a solution of ammonium carbonate added, and the solution gently evaporated nearly to dryness. This is done to separate what little lime may have escaped the first action of the ammonium carbonate, or may have passed through the filter in solution in carbonic acid. If any of the earths soluble in ammonium carbonate existed in the mineral, those now become separated along with the lime.

' A little more water is now added to the contents of the capsule, and the whole thrown on a small filter; the filtrate as well as washings are received in a small porcelain capsule. The liquid contains only the alkalis (as chlorides and nitrates) mixed with a minute quantity of sal-ammoniac. This is evaporated to dryness over a water-bath, and then heated cautiously over the lamp, to drive off what sal-ammoniac may have formed, which is exceedingly minute if the process as pointed out be closely adhered to. It is not absolutely necessary to heat the capsule over the lamp to get rid of the sal-ammoniac, for the little ammonium sulphate which may be formed in the next step is easily removed in the final heating in a platinum vessel.

' On the contents of the capsule, as taken either from the water-bath or as after being treated over the lamp, pure dilute sulphuric acid is poured (1 part acid, 2 water), and the contents boiled for a little time, when all the nitric acid and chlorine in combination with the alkalis will be expelled; the acid solution of the alkalis is now poured into a platinum capsule or crucible, evaporated to dryness, and ignited. In order to ensure complete reduction of the bisulphates to the neutral sulphates, the usual method must be adopted of throwing some pulverised ammonium carbonate into the platinum capsule or crucible, and covering it up so as to have an ammoniacal atmosphere around the salt, which will ensure the volatilisation of the last traces of free sulphuric acid. The alkalis are now in the state of pure sulphates, and may be weighed as such.

' Thus far, the mineral has been supposed to contain no magnesia. If this alkaline earth be present, take the residue as found in the capsule,

dissolve it in a little water, then add sufficient pure lime-water to render the solution alkaline; boil and filter; the magnesia will, in this simple way, be separated from the alkalies. The solution which has passed through the filter is treated with ammonium carbonate in the manner alluded to (page 83), and the process continued and completed as described.

' Conversion of the Sulphates of the Alkalies into Chlorides. The method ordinarily adopted to accomplish this change is to precipitate the sulphuric acid by means of barium chloride, care being taken to avoid the slightest excess of the latter. The annoyance attendant upon this exact precipitation is familiar to all who may have had occasion to make the trial.

' Instead of barium chloride lead acetate is used; a solution of this salt is poured in excess upon the solution of sulphates; warming the latter slightly, the lead sulphate readily separates; the whole can be immediately thrown on a filter and washed; a drop or two of the lead acetate should be added to the filtrate to ensure there being an excess of the lead salt.

' The filtrate is then warmed and sulphuretted hydrogen added; care must be taken to see that there is an excess of sulphuretted hydrogen, a test most readily performed by means of a piece of lead-paper. The liquid is thrown on a filter to separate the lead sulphide; ¹ the filtrate containing the alkalies as acetates is evaporated, and, when nearly dry, an excess of hydrochloric acid is added, and the whole evaporated to dryness over a water-bath, and finally heated to above 250°. A hot solution of the lead chloride can be used instead of the acetate, rendering the addition of hydrochloric acid unnecessary.

' It needs but little experience to convince one of the superiority of this method over that by the barium chloride for converting the sulphates into the chlorides, its principal recommendation being the indifference with which an excess of the lead-salt can be added to precipitate the sulphuric acid, and the subsequent facility with which that excess of lead can be got rid of. It may be well to state that experiments were made to prove the perfect precipitation of the sulphuric acid from the sulphates of the alkalies by salts of lead, and it is only after numerous comparative results that it is now recommended.

' Substitution of Ammonium Chloride for Calcium Fluoride to Mix with Calcium Carbonate for Decomposing the Silicates.—It is mentioned above (page 29) on this subject how calcium carbonate could be rendered as powerful in its decomposing agency on the silicates as caustic potash, the effect being due to the use of some flux, fluoride or calcium chloride being used for that purpose. I have since

¹ ' If lime-water is made, it is well to make it of lime of the best quality, and the first two or three portions of distilled water shaken up should be thrown away, as containing the small amount of alkalies sometimes present in lime.

tested more carefully the merits of the calcium chloride, and for various reasons prefer it to the exclusion of the fluoride. In the first place, it introduces chlorine instead of fluorine into the analysis; and secondly, the fused mass is more easily detached from the crucible, and dissolved by hydrochloric acid.

‘The manner of introducing the calcium chloride into the mixture of mineral and calcium carbonate was a point of some little importance, as from the deliquescent nature of that compound it was inconvenient to weigh and mix it with the calcium carbonate and mineral; these difficulties are obviated by employing *ammonium chloride* to form indirectly the calcium chloride.

‘The process, which appears to leave hardly anything to be desired, is to take 1 part of the finely pulverised mineral, 5 to 6 of calcium carbonate, and $\frac{1}{2}$ to $\frac{3}{4}$ of ammonium chloride;¹ mix them intimately in a glazed mortar, place the mixture in a platinum crucible, and heat to bright redness in a furnace² from 80 to 40 minutes.

‘There is no silicate which, after having undergone this process, is not easily dissolved by hydrochloric acid. For the action of the lime to have been complete, it is not necessary that the mass should have settled down in perfect fusion. The contents of the crucible are dissolved, and the analysis continued as pointed out in the preceding pages.

‘This method ensures the obtaining of every particle of the alkalis in the mineral examined, requiring no more precaution than any good analyst is expected to take in the simplest of his processes; and not the least of the advantages is the ready method of separating all the other ingredients, and the small accumulation of water arising from the little washing necessary.

‘A Speedy Method of Separating the Alkalies directly from the Lime-Fusion, for both Qualitative and Quantitative Determination.—As soon as the fusion with calcium carbonate and sal-ammoniac gave evidence of the mineral being so thoroughly attacked, the question naturally arose as to the condition the alkalis were in after the fusion, and the possibility of dissolving them out by the agency of water alone, at least for the purpose of qualitative determination. Experiments directed to this object soon made it evident that the alkalis might be obtained from any silicate, without resorting to the use of acid as a solvent for the fusion.

¹ ‘The ammonium chloride is best obtained in a pulverulent condition by dissolving some of the salt in hot water, and evaporating rapidly; the greater portion of the ammonium chloride will deposit itself in a pulverulent condition, the water is poured off, and the salt, thrown on bibulous paper, allowed to dry, the final desiccation being carried on in a water-bath, or in any other way with a corresponding temperature.

² ‘An ordinary portable furnace with a conical sheet-iron cap of from 2 to 3 feet high answers the purpose perfectly well, all the requisite heat being afforded by it.

' The mass as it comes from the crucible is placed in a capsule with water, and then heated in a sand-bath or over a lamp for two or three hours, renewing the water from time to time as it evaporates. The mass disintegrates very shortly after being placed in the water. The contents of the capsule are next thrown on a filter, and the water passes through, containing the chloride of the alkali, a little calcium chloride and caustic lime; all else that the mineral may have contained remains on the filter, except baryta and strontia, if they be present in the mineral; but as these oxides are of rare occurrence in silicates, no allusion will be made to them here.

' To the filtrate add ammonium carbonate, and boil for some time, when all the calcium will be precipitated as carbonate; add a few drops of a solution of ammonium carbonate to the hot solution to be sure that all the calcium is precipitated; should this be the case, filter; the filtrate will contain the chlorides of the alkalies and ammonium chloride; it is evaporated to dryness over a water-bath in a small platinum capsule; the capsule is carefully heated to expel the sal-ammoniac, and finally heated to about 400° ; it is then weighed with its contents, and the chlorides, if mixed, separated in any convenient manner. The amount of sal-ammoniac to be expelled is quite small, not equalling the weight of mineral originally employed.

' Nothing in analysis can be simpler or more speedy than this process. Its constant accuracy still lacked some little to render it perfect, as usually an amount of alkali remained behind amounting to from $\frac{1}{10}$ to 1 per cent. of the mineral used, certainly a small quantity, but still too much to be omitted in an accurate analysis. This also must be arrived at, and it can be accomplished in the following manner:—

' After the fused mass has been treated with water, filtered, and washed as above, the filter and its contents are dried; the latter are detached from the filter and rubbed up in a glazed mortar with an amount of sal-ammoniac equal to one-half the weight of the mineral, and reheated in a platinum crucible exactly as in the first instance, treated with water, thrown on a filter and washed, the filtrate added to that from the first fusion, the whole treated with ammonium carbonate and completed as above described.

' This second fusion complicates the method but little, as the residue on the filter readily dries in a water-bath into a powder that is easily detached from the filter, and the small portion adhering to the latter may be disregarded, as the alkalies remaining rarely exceed more than $\frac{1}{100}$ of the whole mass, and, in most instances, not more than $\frac{1}{1000}$. In many analyses made, one fusion sufficed for the entire extraction of the alkalies; but as a few tenths would occasionally remain behind, we preferred the additional fusion to get at that small quantity, and to entitle it to rank as a method by which all but the merest trace of the alkalies could be extracted from the insoluble silicates.

'The proportion of sal-ammoniac added to the calcium carbonate as here recommended was arrived at after numerous experiments. By increasing the sal-ammoniac, and thereby augmenting the amount of calcium chloride formed, the mass fuses more thoroughly, but the water does not disintegrate it as completely as when the ammoniacal salt is less—an object not to be disregarded.

'The advantage of thus estimating the alkalis in insoluble silicates is obvious; the long routine of separating silica, alumina, lime, &c., is done away with; the accumulation of ammonium chloride is very trifling; and lastly, the alkalis are obtained directly in the form of chlorides. The method will vie in accuracy with any other, including the one already mentioned in the first part of this description, and at the same time it is unequalled in simplicity, speed of execution, and constancy of results.

'In examining for alkalis qualitatively one fusion will of course be all that is necessary, and the action of the heat need not be continued more than 30 minutes before filtering. This method will not answer when boracic acid is present in the silicate.' For methods of proceeding in such a case, see the chapter treating on Boron.

In a recent note on the subject of alkalis in silicates Professor Lawrence Smith gives some interesting particulars respecting the presence of rare alkalis in the mineral leucite:—

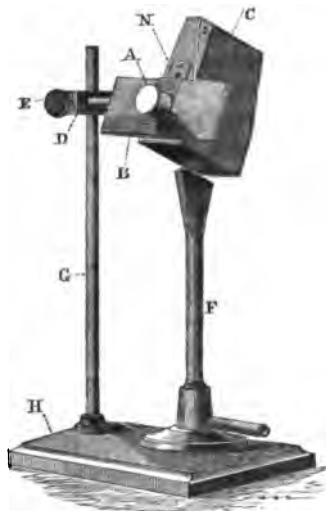
'The specimens of leucite examined came from four localities—Vesuvius, Andernach, Borghetta, and Frescati. They were about as good specimens as are obtained from those localities, although all of them were not equally pure. The alkalis found in each, calculated as potash, were—

Vesuvius	21·85
Andernach	20·06
Borghetta	20·68
Frescati	20·88

'Although they are said to be "calculated as potash," there is a notable quantity of rubidium and cesium present in all the specimens above mentioned. In fact, by the method adopted in testing for these alkalis, abundant indications are obtained of the presence of rubidium and cesium (the last not so readily), even when operating on but $\frac{1}{2}$ a gramme of the mineral. The quantity of these alkalis in leucite is found to be about $\frac{1}{10}$ of 1 per cent. of the entire mineral. Of course it is not at all remarkable that the amount of potash in the different specimens of leucite should be the same; but it is a matter of interest to know that, from whatsoever locality it comes, this minute quantity of rubidium and cesium occurs with it.

22. 'A Special Arrangement for Heating the Crucibles by Gas.—The support and burner, where gas is to be had (as it is in almost all analytical laboratories) are simple in their character, and have been arrived at after a great variety of experiments with gas furnaces. The

figure here given illustrates the stand, burner, crucible, &c., and is about one-sixth the natural size. H is the stand with its rod, G. D is a brass clamp, with two holes at right angles to each other; having two binding screws, it slides on the rod, G; the second hole is for a round arm attached to B, the binding screw, E, fixing it in any position. B is a plate of cast-iron, 5 to 6 millimetres thick, 10 to 11 centimetres long, and $4\frac{1}{2}$ centimetres broad, having a hole in its centre large enough to admit the crucible to within about 15 millimetres of the cover without binding. A is the crucible already referred to, which is made to incline a few degrees downwards, by turning the plate of iron that supports it. C is a chimney of sheet iron, 8 to 9 centimetres long, 10 centimetres high, the width at the bottom being about 4 centimetres at one end and about 3 centimetres at the other end. It is made with the sides straight for about 4 centimetres, then inclines towards the top, so as to leave the width of the opening at the top about 1 centimetre. A piece is cut out of the front of the chimney of the width of the diameter of the hole in the iron support, and about 4 centimetres in length, being semicircular at the top, fitting over the platinum crucible. Just above this part of the chimney is rivetted a piece of sheet iron in the form of a flattened hook, N, which holds the chimney in place by being slipped over the top of the crucible support; it serves as a protection to the crucible against the cooling effects of the currents of air. F is the burner, which has been described in an article on flame heat in the *American Journal of Science*, November, 1870, p. 841, the upper opening of which is a slit from $1\frac{1}{2}$ to 2 millimetres in width, and from 3 to 4 centimetres long, and when used is brought within about 2 centimetres of the lowest point of the crucible, the end of the flame just playing around the lower end of the crucible. The gas enters the lower part of the burner by two small holes of $\frac{1}{16}$ of an inch, furnishing at 1 inch pressure about $5\frac{1}{2}$ cubic feet of gas per hour. The precaution must be observed, already referred to, of heating the crucible at first gently.

FIG. 1.¹

28. 'It is surprising to see the effect produced by this simple burner

¹ These burners and stands, as well as the platinum crucibles, made according to Professor Lawrence Smith's pattern, can be obtained of Messrs. Johnson and Matthey, Hatton Garden.

as here used ; 8 grammes of precipitated calcium carbonate can be decomposed to within 2 or 3 per cent. in one hour, and when mixed with silica or a silicate, in a very much shorter space of time, although in my analyses I employ one hour, as it requires no attention after the operation is once started. This form of furnace and crucible is found to be convenient for other operations.

24. ' Although the details given here are lengthy, the time occupied in the analysis is short and the precautions necessary are of a simple character, so much so that results obtained by students on beginning chemical analysis have been found by me reliable, and less variable on the alkalis of the silicates than of any of the other constituents of this class of bodies. I have often made good alkali determinations in three hours from the commencement of the operations, hastening the evaporations by more direct application of heat, which, of course, requires close watching.

25. ' It is a common practice, when a silicate comes under my examination that is not easily made out by its physical properties, to make at once an alkali determination, which often indicates at once what it is if it be a known silicate. If not, the alkali determination serves as one step in its examination.'

Estimation of Alkalies in Fire-Clays and other Insoluble Silicates.

Mr. G. Gore, F.R.S., has described a modification of the hydrofluoric process of treating silicates, which had been found useful when only the alkalies are required. An intimate mixture of the finely powdered fire-clay, barium nitrate, and barium fluoride is projected into a heated crucible ; when all the mixture has been thrown in, the crucible is covered and gradually heated in a furnace until the contents are completely melted ; the mixture is poured into a cast-iron vessel, and immediately covered over. The resulting fused mass is finely powdered, digested with sulphuric acid, evaporated to dryness, and afterwards treated in the usual manner. The results of analyses made in this manner agree with those obtained by the hydrofluoric acid process.

In the chapter on Silicates will be found other methods of analyses by which the alkalies may be separated and estimated ; but the processes are mostly devised for the simultaneous estimation of many other substances, whilst at the same time they are not so simple as those here given.

AMMONIA.

Ammonia, Nessler's Test for.—This test is of great value in water analyses and other cases where the ammonia is present in minute quantities only. Mr. Hadow, Dr. W. A. Miller, Professor Frankland, and Dr. Armstrong have introduced useful modifications

into the original process. The following process, which has been found to answer perfectly, is based upon the descriptions of the above chemists.

Make a concentrated solution of an ounce or more of corrosive sublimate; having dissolved $2\frac{1}{2}$ ounces of potassium iodide in about 10 ounces of water, add to this the mercurial solution until the mercury iodide ceases to be dissolved on agitation; next dissolve 6 ounces of solid hydrate of potash in its own weight of water, and add it gradually to the iodised mercurial solution, stirring whilst the mixture is being made; then dilute the liquid with distilled water till it measures one quart. When first prepared it usually has a brown colour of greater or less intensity, owing to the presence of a little ammonia; but if set aside for a day or two it becomes clear and nearly colourless; the clear liquid may then be decanted for use. For a litre of the test liquid of equal strength 62.5 grammes of potassium iodide and 150 grammes of solid caustic potash will be required. About 50 grains (8 c.c.) of this solution are drawn off by a marked pipette and added to one-half of a solution or distillate to be tested for ammonia; if no ammonia be present the mixture remains colourless, but if ammonia be present the liquid will assume a yellowish tinge of greater or less intensity. The liquid will remain clear if the ammonia do not exceed $\frac{1}{1000}$ of a grain in the 5 ounces, or about 0.25 milligramme in 125 grammes of the distillate. The quantity of ammonia in such a case may be very accurately estimated in the following manner:—A solution of sal-ammoniac is prepared, containing 3.17 grains of the salt in 10,000 grains of water (or 0.816 gramme of salt per litre), which is equivalent to $\frac{1}{10000}$ of a grain of ammonia in each grain of this solution, or 0.1 gramme in 1 litre. Suppose that a tint is obtained in the distilled liquid, which experience leads the observer to estimate, say, at $\frac{5}{10000}$ of a grain; 50 grains of the standard sal-ammoniac solution are placed in a beaker similar in size to that used for the distillate under trial, then diluted with 5 ounces of distilled water previously ascertained to be free from ammonia (an impurity not unfrequently met with in the first portions of water which come over in distillation); lastly, 50 grains of the mercurial test liquor are added.

If the tint coincides in intensity with that furnished by the distillate which has received an equal quantity of the mercurial test, the amount of ammonia may be considered to correspond with that taken in the liquid for comparison. If the distillate appear to have a deeper or a paler tint, a second approximative trial with a larger or a smaller quantity of sal-ammoniac must be made, and so on until the operator is satisfied that the tints coincide. On multiplying the number of grains of sal-ammoniac solution employed by 8, the product will give in $\frac{1}{10000}$ of a grain the quantity of ammonia per gallon in the water under examination. Suppose that the observer estimates the amount of ammonia in the 125 c.c. on which he is operating, at 0.25

milligramme, he takes 2.5 c.c. of the sal-ammoniac solution, and dilutes it with distilled water to 125 c.c.; he then adds 3 c.c. of the mercurial liquor, and compares it with the tint produced in the distillate by a like addition of the mercurial test. If the two tints correspond, multiply by 2 the number of c.c. of sal-ammoniac solution required, and the number obtained will give the proportion of ammonia per litre in tenths of a milligramme. When the quantity of ammonia exceeds the $\frac{1}{30}$ of a grain per gallon, or 0.6 milligramme per litre, it is necessary to determine the amount by neutralisation.

Unless the amount of ammonia obtained by distillation alone, or with sodium carbonate, be considerable (about 0.01 part in 100,000 parts of water) this modification of Nessler's process is all that could be desired for its accurate determination. But if a larger proportion than this be obtained in a potable water, the presence of urea may be suspected, and it becomes necessary to make the Nessler ammonia test directly in the original water without the intervention of distillation. For this purpose, however, the water should be colourless, and free from calcium and magnesium carbonates. Any tint which is appreciable in a stratum 6 or 8 inches thick would obviously vitiate the result of a colour-test, whilst, if calcium or magnesium carbonate be present, the addition of the Nessler solution will infallibly produce turbidity; moreover, we find that the slightest opalescence in the water, under these circumstances, is absolutely incompatible with an accurate determination. Both these difficulties may be effectually removed by adding to the water, first, a few drops either of ferric perchloride or of aluminium chloride in solution, and then a few drops of a solution of sodium carbonate, so as to precipitate iron sesquioxide or alumina. The precipitate completely decolourises the water, and no turbidity is caused by the subsequent addition of the Nessler solution; but, unfortunately, the precipitate carries down with it an amount of ammonia which, in the case of the iron sesquioxide, sometimes amounts to one-third of the total quantity present. Remembering the beautiful blue-green tint—the natural colour of absolutely pure water—which is presented by a reservoir of water that has been softened by Clarke's process, Messrs. Frankland and Armstrong tried upon peaty water the effect of precipitating in it calcium carbonate, and found that the decolouration was as complete as could be desired, and that no appreciable amount of ammonia was carried down with the precipitate. The amount of calcium carbonate present in a coloured water is rarely sufficient to enable the operator to carry out this reaction with sufficient rapidity and completeness; it is therefore best in all cases to add a few drops of a concentrated solution of calcium chloride to half a litre of the water. The subsequent addition of a slight excess of sodium carbonate then produces a copious precipitate of calcium carbonate, which should be allowed to subside for half an hour before filtration. 100 c.c. of the filtrate is a convenient quantity to take for the

direct Nessler determination of ammonia. To this volume of the filtrate 1 c.c. of the Nessler solution is added, and the colour observed as above described. By this direct process, the ammonia in fresh urine can be readily estimated; for this purpose 5 c.c. of the urine should be diluted with 95 c.c. of water free from ammonia. Known quantities of ammonia, added in the form of ammonium chloride to urine, can be determined with great accuracy.

The colour observations of the Nessler determination are best made in narrow glass cylinders, of such a diameter that 100 c.c. of the water to be tested form a stratum about 7 inches deep. The depth of tint is best observed by placing these cylinders upon a sheet of white paper near a window, and looking at the *surface* of the liquid obliquely.

Estimation of Ammonia in Gas Liquor.

Mr. T. E. Davis considers that the direct titration of liquor with normal sulphuric acid and calculation into ammonia would be a test sufficient to base a contract upon; and for the guidance of a manufacturer, and for all practical purposes, it may be looked upon as correct. Moreover, each test does not take five minutes, whereas the distillation process takes the best part of an hour.

The titration method of testing is as follows:—Into a flask of about 800 c.c. capacity 10 c.c. of the sample to be tested are run in, and into this 15 c.c. of normal sulphuric acid. The contents of the flask are then raised to boiling over a naked flame, a few drops of litmus added and titrated back with normal soda. The number of c.c. of soda used are deducted from the 15 c.c. of acid employed, the result multiplied by 17 and divided by the specific gravity of the liquor. The result thus obtained represents the percentage of ammonia contained in the liquor. An example will make this clear:—10 c.c. of a liquor at 5° T. (sp. gr. = 1025), boiled with 15 c.c. normal acid, required 5 c.c. normal soda to neutralise it, consequently the sample contains 1·658 per cent. NH_3 ; thus—

$$\frac{(15 - 5) \times 17}{1025} = 1\cdot658$$

Now as to the valuation. Suppose we consider 10s. per unit of NH_3 per ton to be fair value, then the above sample would be worth $1\cdot66 \times 10\cdot5 = 17s. 5d.$ per ton. Such a system would induce gas managers to make the liquor as strong as possible, and ammonia manufacturers would do well if they were to refuse a contract for liquor containing less than 1 per cent. of NH_3 ; for if below this—unless the liquor were given them—they would barely clear expenses of manufacture.

Ammonium Chloride in Analysis.—For the best method of removing the ammonium chloride which unavoidably accumulates in the process of analysis, see *ante*, page 88.

CHAPTER II.

BARIUM, STRONTIUM, CALCIUM, MAGNESIUM.

Indirect Estimation of Barium, Strontium, and Calcium.

THE estimation of these three earthy metals is generally effected after they are separated from each other. These separations can be dispensed with if an indirect method be employed, thereby avoiding the loss attendant upon different separations, and materially hastening and simplifying the whole estimation. The following indirect method, which is very successful for the estimation of these three metals, may also be employed in the presence of magnesium.

In the first place, the calcium, strontium, and barium must be precipitated as carbonates, by means of ammonium carbonate and hydrate. It must be borne in mind that in a liquid containing much sal-ammoniac or ammonium nitrate neither calcium, strontium, nor barium can be completely precipitated by ammonium carbonate, so that, after filtering, it is possible, by means of sulphuric acid or ammonium oxalate, to recognise a more or less considerable quantity. The cause of this is, that ammoniacal salts of strong acids have a solvent action upon calcium carbonate, and this action is still stronger upon the strontium and barium carbonates. Should, on the other hand, ammonium acetate or carbonate be used, instead of sal-ammoniac or ammonium nitrate in solution, the precipitation of the three bases by ammonium carbonate will be so complete that it will be impossible to discover in the filtrate, by means of the before-mentioned reagents, any traces of calcium, strontium, or barium.

In order to have in solution no other ammoniacal salts than acetate and carbonate, it will suffice to add to the tolerably neutral solution as much sodium acetate as there is supposed to be sal-ammoniac or ammonium nitrate held in solution, and then to supersaturate with ammonia and ammonium carbonate, and, after a short digestion, to cool the solution; the carbonated alkaline earths which have in this manner been completely precipitated are now filtered off.

Digestion is not absolutely necessary here; it only serves to render those deposits granular which would otherwise be voluminous. On the other hand, in order to obtain complete precipitation, it will be necessary to reduce the whole to the ordinary temperature before filtering, because hot ammonium acetate has a solvent action upon

carbonated alkaline earths, although in a far less degree than sal-ammoniac.

A certain degree of dilution of the ammoniacal salt is to be recommended; in any case, the solution must not be more concentrated than in the proportion of one part of salt to twenty of water.

Sodium carbonate may be substituted for the acetate, in order to decompose the sal-ammoniac; but if, at the same time, magnesium be held in solution, the presence of a large quantity of an ammonium salt of stronger acid than carbonic will be necessary, in order that it may not be deposited with the alkaline earths. For this purpose, the addition of sodium acetate is eminently suitable, because the ammonium acetate thus formed (as with oxygenated ammonium salts generally) prevents the precipitation of the magnesium much more than sal-ammoniac does, without, as before remarked, dissolving barium, strontium, or calcium.

In the presence of magnesium, a too great excess of ammonium carbonate must be avoided as a reagent, in order to hinder the formation of ammoniacal magnesium carbonate, which is difficult to dissolve. After these precautionary measures, the barium, strontium, and calcium having been separated, the precipitate is washed, filtered, dried, heated, and weighed; it is then dissolved in a measured quantity of normal hydrochloric acid and estimated. This is done (after removing the carbonic acid by heat from the diluted solution, which is coloured with litmus) by estimating with normal standard ammonia solution the amount of hydrochloric acid which had been required to transform the three carbonates into chlorides. The solution is now mixed with a known amount of potassium bichromate, caustic ammonia being added in excess, to precipitate all the barium, so that no trace of it may be detected in the acidulated filtrate, by potassium fluosilicate and alcohol.¹ The barium chromate is filtered off and washed until lead acetate ceases to give a yellow precipitate in the filtrate; in the solution the excess of chromic acid is determined according to the usual process, with a standard solution of iron protosulphate; and the amount of baryta is then obtained, according to the formula—

$$\begin{array}{l} \text{Chromic acid} \times 1.527 = \text{Baryta,} \\ \text{or} \quad \text{Chromic acid} \times 1.964 = \text{Barium carbonate.} \end{array}$$

If, on the one hand, the amount of barium carbonate thus obtained be deducted from the weight of the three carbonates, and, on the other, the amount of hydrochloric acid answering to the baryta be calculated, the difference between this amount of hydrochloric acid and the amount found, will be the quantity of hydrochloric acid which corresponds to

¹ Pure barium chloride solution produces no turbidity when, after the precipitation of baryta by potassium chromate and ammonia, the filtrate is mixed with sulphuric acid. It is, of course, assumed that the reagents employed in precipitation are quite free from sulphuric acid.

the united weight of the calcium and strontium carbonates, which has just been calculated.

The amount of calcium and strontium carbonates is obtained as follows:—Calculate the amount of calcium carbonate (which is equivalent to the known quantity of hydrochloric acid) contained in the excess of calcium and strontium carbonates, deduct this from the weight of the two carbonates, multiply the remainder by the constant factor $8\frac{1}{2}$, and the product will then be the required quantity of strontium carbonate; this, when again subtracted from the united weight of both salts, yields, as its remainder, the quantity of calcium carbonate. The constant factor, $8\frac{1}{2}$, is obtained by the following calculation:—

	Calcium carbonate =	100
	Strontium carbonate =	148
	Calcium and strontium carbonates =	248
hence	2 eqs. of calcium carbonate =	200

and this subtracted from the equivalent of strontium carbonate leaves 48, and 148 divided by 48 = $8\frac{1}{2}$.

This method of estimating these three earthly metals always yields satisfactory results. It is quickly carried out, and is very exact, because the precipitations are all perfect, and the two volumetric estimations involved in the method admit of great accuracy. Moreover, the troublesome and somewhat uncertain separation of the strontium and calcium with a concentrated solution of ammonium sulphate, which is very inconvenient in estimating the calcium, is avoided.

In the absence of strontium, either precipitate the calcium and barium as carbonates, estimating the precipitate alkalimetrically; or precipitate the barium as sulphate, and the calcium as carbonate, by digesting the solutions of both with a mixture of three parts of potassium sulphate and one part of potassium carbonate; weigh the dried and ignited precipitate, and estimate the calcium carbonate alkalimetrically.

Estimation of Calcium.

Dr. A. Cossa has determined the accuracy of estimating calcium as quicklime or caustic lime, instead of weighing it as calcium carbonate. The experiments were made—(1) With pure calcium oxalate previously dried at 100° ; (2) with calcium carbonate precipitated from a solution of pure calcium chloride by means of pure sodium carbonate; (3) with pure native calcium carbonate. The result of an average of three experiments with No. 1 is 0.07 per cent. too low; with No. 2, 0.85 per cent. too low; with No. 3, 0.27 per cent. too high.

To avoid the inaccuracy and loss of time nearly always resulting from the ordinary method of determining calcium, viz. by strongly heating the precipitate of calcium oxalate, and converting the same into carbonate by repeatedly moistening with solution of ammonium carbonate, Mr. Scott recommends the weighing the precipitate as

sulphate instead. The addition of sulphuric acid, or even of ammonium sulphate alone, to caustic lime is hardly a safe operation, in an analytical point of view, if the mass in the crucible is at all bulky, but by using the following solution no inconvenience is experienced. Three parts of pure *liquor ammonia* of the ordinary strength should be just neutralised with pure sulphuric acid (previously diluted with its bulk of water), and two parts of the ammonia solution added. In each ounce of the fluid thus obtained 10 grains of ammonium chloride must be dissolved; the whole may then be filtered into a small reagent bottle and appropriately labelled. It must, of course, entirely volatilise when heated on platinum foil. In this manner the calcium is weighed as *sulphate*, which may be strongly ignited without change, *one weighing* therefore being sufficient.

Calcium Phosphates.

The commercial estimation of superphosphates is given in the chapter on Phosphoric Acid. The following process, recommended by Professor F. Wöhler, for the analysis of apatite and similar phosphates, will be found to be one of the most trustworthy:—Dissolve the mineral in nitric acid in a capsule, and then add pure mercury in such a quantity that when the acid is saturated with it there still remains a portion of mercury undissolved. Evaporate the mixture on the water-bath to complete dryness. If a slight odour of nitric acid is still disengaged, add more water, and evaporate again to dryness, so as to get rid of it completely; then extract with water, place it on the smallest possible filter, and well wash the residue, which contains all the phosphoric acid.

Besides the excess of mercury the filtrate contains all the calcium. With hydrochloric acid precipitate the mercury proto-salt. As a little mercuric binoxide may have been formed, precipitate the solution with ammonia. If the mineral contains iron or other bases precipitable with ammonia, these remain after calcining the last precipitate. The solution is rapidly filtered with as little exposure to the air as possible, and the calcium in it precipitated with ammonium oxalate.

The filter, which, besides the excess of mercury, contains phosphoric acid, is well dried, and the whole is placed in a platinum crucible and mixed with potassium and sodium carbonates. The crucible is then heated to a temperature below redness, under a chimney with a good draught, until all the mercury is volatilised, after which it may be heated to redness and the contents fused. Then dissolve in water, add an excess of hydrochloric acid, and precipitate the phosphoric acid with ammonia and magnesium sulphate.

To estimate the chlorine, dissolve a known weight of the mineral in dilute nitric acid,¹ and precipitate the chlorine with silver nitrate.

¹ Certain brown apatites leave as a residue a small quantity of a crystalline powder, which is cryptolite (cerous phosphate).

Some kinds of apatite contain a small quantity of fluorine. When it is desired to ascertain the presence of this body, finely powder the mineral, and then mix it in a platinum crucible with concentrated sulphuric acid; cover the crucible with a piece of glass, coated with wax, and having characters traced on it with the point of a needle. Then heat the crucible, taking care not to melt the wax. If fluorine is present, the characters will be found engraved on the glass when the wax is removed. The amount of fluorine present may be deduced from the loss of weight obtained in the complete analysis.

Separation of Calcium from Strontium.

The best process is that originally devised by Stromeyer, based upon the solubility of calcium nitrate in absolute alcohol and the insolubility therein of strontium nitrate, but adding an equal volume of ether to the alcohol. A mixture of alcohol and ether does not dissolve more than $\frac{1}{8000}$ part of strontium nitrate, whilst it dissolves calcium nitrate perfectly.

A similar separation may be effected by ammonium sulphate, in which calcium sulphate is soluble, whilst strontium sulphate remains unaffected. The proportions to employ are, 50 parts of ammonium sulphate and 200 parts of water to 1 of strontium sulphate. There is then formed a soluble double salt, which resembles potassio-gypsite (calcium and potassium sulphate). This process is, however, less delicate than that of Stromeyer.

Detection of Calcium in the Presence of Strontium and Barium.

An ammoniacal solution of arsenious acid gives a precipitate of calcium arsenite in neutral calcium salts. Under similar circumstances barium and strontium give no precipitate.

Separation of Strontium from Barium.

When in the form of sulphates, prolonged digestion with a cold solution of ammonium carbonate will convert the strontium into carbonate, whilst it has no action on the barium. Boiling the solution, or employing sodium carbonate, is not so effectual. Finely pulverise the mixed salts, wash thoroughly with water, and treat with nitric acid. The strontium will dissolve as nitrate and leave the residue of the barium sulphate. Barium and calcium may be separated in a similar manner.

MAGNESIUM.

Applications of Metallic Magnesium.—The magnesium which is now met with in commerce in the form of ribbon, wire, and rod, possesses properties which render it of great value in some chemical operations.

When magnesium is added to a slightly acid solution of iron, zinc, cobalt, or nickel salts, an evolution of hydrogen takes place, and these metals are respectively precipitated in the metallic state. When washed, dried, and compressed, the precipitated metals possess great brilliancy and dissolve completely in acids. The iron, cobalt, and nickel so obtained are highly magnetic. Besides these metals, magnesium precipitates gold, silver, platinum, bismuth, tin, mercury, copper, lead, cadmium, and thallium.

When magnesium is put into water containing a little common salt, sal-ammoniac, or dilute acid, very pure and inodorous hydrogen gas is evolved. Owing to the high electromotive force of magnesium, and its low equivalent, it would be decidedly the best positive element for galvanic batteries could it be produced at a cheap rate.

When magnesium is introduced into an acid solution containing arsenic or antimony, these metals are not precipitated, but combine with the evolved hydrogen, and pass off as arseniuretted or antimoniuiretted hydrogen. Owing to the great purity of the distilled magnesium of commerce, and its freedom from silicium and poisonous metals, it is invaluable to the toxicologist, and should always be used in Marsh's apparatus instead of zinc, for the evolution of hydrogen. Further particulars as to the special employment of magnesium for this purpose will be found in the chapter treating on Arsenic.

Determination of Magnesium as Pyrophosphate.

Mr. R. W. Emerson McIvor strongly recommends the process of Dr. Gibbs, who substitutes microcosmic salt for ordinary sodium phosphate. He heated the mixed solution of magnesium sulphate and ammonium chloride to the boiling-point, and precipitated the magnesium from the boiling liquid by adding the ammonium phosphate solution. After having been allowed to cool, ammonium hydrate was added, and the whole allowed to stand for twenty-four hours. The precipitate of magnesium ammonio-phosphate was then collected upon a filter, dried at 100° C., ignited, and weighed as magnesium pyrophosphate in the usual manner. As magnesium is a substance which analysts have frequent occasion to estimate, Dr. Gibbs' suggestions are well worthy of their consideration.

Separation of Magnesium from Calcium.

The method of separating calcium and magnesium by means of ammonium oxalate does not succeed when only a very small quantity of calcium is present. In such a case the calcium is either not precipitated at all, or but very incompletely. Free ammonia also tends to hinder the precipitation, and, when it has evaporated, crystals are obtained, which consist of calcium oxalate with magnesium oxalate, and the liquid still contains calcium. A better result, Scheerer says,

Some kinds of apatite contain a small quantity of fluorine. When it is desired to ascertain the presence of this body, finely powder the mineral, and then mix it in a platinum crucible with concentrated sulphuric acid; cover the crucible with a piece of glass, coated with wax, and having characters traced on it with the point of a needle. Then heat the crucible, taking care not to melt the wax. If fluorine is present, the characters will be found engraved on the glass when the wax is removed. The amount of fluorine present may be deduced from the loss of weight obtained in the complete analysis.

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MAGNESIUM.

Applications of Metallic Magnesium.—The magnesium which is now met with in commerce in the form of ribbon, wire, and rod, possesses properties which render it of great value in some chemical operations.

When magnesium is added to a slightly acid solution of iron, zinc, cobalt, or nickel salts, an evolution of hydrogen takes place, and these metals are respectively precipitated in the metallic state. When washed, dried, and compressed, the precipitated metals possess great brilliancy and dissolve completely in acids. The iron, cobalt, and nickel so obtained are highly magnetic. Besides these metals, magnesium precipitates gold, silver, platinum, bismuth, tin, mercury, copper, lead, cadmium, and thallium.

When magnesium is put into water containing a little common salt, sal-ammoniac, or dilute acid, very pure and inodorous hydrogen gas is evolved. Owing to the high electromotive force of magnesium, and its low equivalent, it would be decidedly the best positive element for galvanic batteries could it be produced at a cheap rate.

When magnesium is introduced into an acid solution containing arsenic or antimony, these metals are not precipitated, but combine with the evolved hydrogen, and pass off as arseniuretted or antimonuretted hydrogen. Owing to the great purity of the distilled magnesium of commerce, and its freedom from silicium and poisonous metals, it is invaluable to the toxicologist, and should always be used in Marsh's apparatus instead of zinc, for the evolution of hydrogen. Further particulars as to the special employment of magnesium for this purpose will be found in the chapter treating on Arsenic.

Determination of Magnesium as Pyrophosphate.

Mr. R. W. Emerson McIvor strongly recommends the process of Dr. Gibbs, who substitutes microcosmic salt for ordinary sodium phosphate. He heated the mixed solution of magnesium sulphate and ammonium chloride to the boiling-point, and precipitated the magnesium from the boiling liquid by adding the ammonium phosphate solution. After having been allowed to cool, ammonium hydrate was added, and the whole allowed to stand for twenty-four hours. The precipitate of magnesium ammonio-phosphate was then collected upon a filter, dried at 100° C., ignited, and weighed as magnesium pyrophosphate in the usual manner. As magnesium is a substance which analysts have frequent occasion to estimate, Dr. Gibbs' suggestions are well worthy of their consideration.

Separation of Magnesium from Calcium.

The method of separating calcium and magnesium by means of ammonium oxalate does not succeed when only a very small quantity of calcium is present. In such a case the calcium is either not precipitated at all, or but very incompletely. Free ammonia also tends to hinder the precipitation, and, when it has evaporated, crystals are obtained, which consist of calcium oxalate with magnesium oxalate, and the liquid still contains calcium. A better result, Scheerer says,

is obtained by converting the alkaline earths into neutral sulphates, and adding alcohol to the aqueous solution until a persistent cloudiness is produced. After some hours all the calcium sulphate is deposited. When too much alcohol has been used, some of the magnesium sulphate is deposited as well; it is sufficient then to redissolve the sulphates in water and precipitate a second time with alcohol, or the calcium may now be thrown down by the ammonium oxalate. The magnesium, not being in excess, no longer hinders the precipitation.

As regards the analysis of dolomite, Dr. A. Cossa states, that when care is not taken to redissolve the precipitate of calcium oxalate first obtained, and reprecipitate this a second time, it is always so contaminated with magnesium oxalate or magnesium ammonio-oxalate, that the quantity of calcium found as carbonate may be 0.62 per cent. in excess of what it ought to be, while the loss for magnesium carbonate may even be as high as 0.78 per cent.

When, in the ordinary course of qualitative analysis, ammonium carbonate is used to separate calcium from magnesium, unless the former metal is present in notable proportion to the latter, a very insoluble double magnesium and ammonium carbonate always accompanies the calcium carbonate if this is allowed sufficient time to form. If much magnesium and no calcium be present, the magnesium precipitate still falls after awhile. Both metals are precipitated by this reagent, the only difference being that the calcium precipitate forms somewhat earlier than the magnesium precipitate. Calcium, therefore, can only be separated from magnesium by this reagent by fractional precipitation, which necessarily involves loss of substance; and, in qualitative examination, the method is sure to mislead when the proportion of calcium present is small, unless it is controlled by other methods. The same remarks apply, in substance, to the method of precipitation by ammonium oxalate. Within a trace the whole of the magnesium present in a considerable quantity of solution of magnesium chloride can be precipitated simply by successive additions of ammonium oxalate—the solution being concentrated to its original bulk after the last addition of the reagent. Yet, in working with this reagent, the rule is, that enough of it must always be added to transform all the magnesium salt into oxalate, since calcium oxalate is soluble in solution of magnesium chloride. That some magnesium salt must precipitate with the calcium salt under such conditions is obvious: and that it does so is well known, and is, though incompletely, provided for by the direction being given to repeat the process upon the precipitate first obtained. This process, therefore, is also one of fractional precipitation, and for it to approach success, the operator must know pretty nearly beforehand how much calcium, in proportion to the magnesium present, he has to deal with.

Mr. Edward Sonstadt has discovered that in common sodium tung-

state we possess a test for calcium which is probably equal in delicacy and in certainty to that of chlorine for silver, or of sulphuric acid for barium, and on this discovery he has based an excellent method for the separation of magnesium from calcium.

Mr. Sonstadt gives the following details respecting the manipulation required in separating calcium from magnesium by sodium tungstate that experience has shown to be necessary. It is convenient to have the solution of the magnesium and calcium salts made somewhat alkaline by ammonia, but a very large quantity of this, as well as of ammoniacal salt, is to be avoided. The beaker in which the precipitation is to be effected should, while perfectly dry and warm, be rubbed within by chamois leather on which a drop or two of fine oil (such as is used for oiling balances) has been put. If this precaution be not taken it will be found impossible to detach the precipitate of calcium tungstate from the sides and bottom of the vessel. A considerable excess of the reagent is not necessary, but, if it occur, is not material. If, on addition of the reagent, a white flocculent precipitate forms immediately, it is well to add a few drops of ammonia, when the flocculent precipitate will redissolve; but, if it does not redissolve after warming, there is some other element present, which, if ordinary Epsom salts are used, will probably be manganese. The calcium tungstate precipitate is very dense; it forms slowly in very dilute solutions, and, in all cases, several hours should be allowed for it to form. The solution should be warmed meanwhile, but must not be allowed to boil. The precipitate must be washed till the filtrate shows no cloudiness on standing with silver nitrate when the salts are chlorides; or, if they are sulphates, till barium chloride gives no cloudiness. The precipitate must then be further washed with dilute solution of ammonia, but these washings need not be saved. The filter should be burnt separately, after the precipitate is cleared from it as nearly as possible. After the ignited precipitate is weighed, a little strong solution of ammonia should be poured upon it, and allowed to stand for a while, when the ammonia is decanted, and supersaturated with acid. If a precipitate falls after a time, the calcium tungstate precipitate should (without being removed from the crucible) be allowed to stand for some hours with more ammonia; it is then washed by decantation, again ignited, and weighed. The ignited precipitate should be perfectly white.

The filtrate containing the magnesium salt and sodium tungstate may be at once precipitated by sodium phosphate in the usual way; but if this is done much washing is required to get rid of the little tungstic acid that adheres obstinately to the precipitate. It is better, especially when a great excess of the reagent has been used, to first precipitate the tungstic acid by a considerable excess of hydrochloric acid, and boil until the precipitate becomes dense and intensely yellow. The solution is then filtered, supersaturated with ammonia,

and the magnesium precipitated in the usual way ; but, even in this case, it is better to wash lastly with stronger ammonia solution than ordinary.

Mr. E. Sonstadt also separates calcium and magnesium in the following manner. He finds that calcium iodate is not sensibly soluble in a saturated solution of potassium iodate, whereas magnesium iodate is not precipitated from solution in any degree by potassium iodate. If to 10 or 12 c.c. of a saturated solution of potassium iodate a few drops are added of solution of calcium sulphate, and after two hours the liquid is filtered and ammonium oxalate added to the filtrate, a slight opalescence appears after a while, due to the presence of a trace of calcium. But if the potassium iodate solution to which the calcium salt was added, is allowed to stand twenty hours, and is then filtered and ammonium oxalate added to the filtrate, not the slightest opalescence appears, even after many hours. A slight crystallisation takes place, owing to a diminution of the solubility of the potassium iodate by the presence of ammonium oxalate, but the crystals entirely disappear, leaving the solution perfectly limpid on addition of a very small proportion of water. The precipitation of calcium by saturation of the solution with potassium iodate does not appear to be affected by the presence of alkali and magnesium salts, in whatever proportion these may be present. If, for instance, a small quantity, as a decigramme, of ordinary Epsom salts is dissolved in the least possible quantity of water, and four or five times its bulk of a saturated solution of potassium iodate is added, after a few hours a crystalline precipitate forms, which may be collected on a filter, washed with solution of potassium iodate, dissolved off the filter with dilute hydrochloric acid, and minute as the quantity of calcium present is, it may be shown immediately by the precipitate falling on addition of ammonia and ammonium oxalate to the strongly acid filtrate.

In separating calcium from magnesium by precipitation of the former by potassium iodate it is obviously important, in view of the subsequent determination of the magnesium, to know if the presence of potassium iodate hinders the precipitation of magnesium as magnesium-ammonium phosphate. So far from this being the case, it is found that the double phosphate is even less soluble in a saturated solution of potassium iodate containing some free ammonia than it is in a mixture of two parts ordinary 'liquor ammoniæ' with one part of water. Thus the addition of solution of potassium iodate to the ordinary liquid containing phosphate of an alkali and much free ammonia, over precipitated magnesium-ammonium phosphate, renders the fluid at once opalescent, and occasions an additional precipitation of magnesium salt.

Mr. Sonstadt says that he has never met with a specimen of any magnesia or magnesium salt in commerce, although sold as chemically pure, that did not contain a very sensible portion of calcium. The

only available source of a magnesium salt free from calcium is distilled magnesium.

Dr. Mohr also uses microcosmic salt in precipitating magnesia after lime from an ammoniacal solution which has been kept clear by means of sal-ammoniac.

In separating magnesium salts from lime, ferric oxide, and the alkalis, H. Hager mixes the finely-powdered sample with 10 parts of glycerine and a little water, and adds 40 to 50 parts of solution of oxalic acid at 5 per cent. Calcium and magnesium oxalates are both formed, the former remaining undissolved, whilst the magnesium salt passes into solution. After standing for half an hour the calcium oxalate is collected upon a filter, washed, and determined as usual. The filtrate is boiled in a flask for five to eight minutes, filtered boiling, and the precipitate is dried, and weighed as magnesia.

In a solution containing calcium and magnesium salts the liquid is first mixed with glycerine, a sufficiency of ammonium oxalate is added, the liquid is strongly acidified with oxalic acid, and the process is completed as above.

Magnesium can also be precipitated as an oxalate in presence of ferric oxide by adding glycerine, ammonium oxalate and oxalic acid, and then boiling. In order to determine the ferric oxide in the filtrate it is heated to a boil along with ammonium carbonate, evaporated to dryness, the glycerine extracted with alcohol, the insoluble residue treated with hot ammoniacal water, and the ferric hydroxide is collected upon a filter.

For separating magnesia from the alkalis the hydrochloric solution is boiled with ammonium oxalate and oxalic acid, and filtered at a boil.

The following method shows whether in calcined magnesia or magnesium carbonate the proportion of lime exceeds a certain limit :— 0·1 gramme of calcined magnesia or 0·25 gramme of the carbonate must be well shaken up in a test-tube with a solution of oxalic acid at 5 or 10 per cent. Perfectly pure preparations dissolve in the first minute, and the solution remains clear for five minutes ; in presence of lime the solution is turbid. In the latter case the agitated turbid liquid is poured into a test-tube 1·25 centimetre wide, and an ink-line upon paper 1 millimetre in breadth is examined through the column of liquid. If the line is perceptible, the preparation of lime in the calcined magnesia does not exceed 0·25 per cent., and that in the carbonate 0·1 per cent.

Separation of Magnesium from Potassium and Sodium.

In the following method phosphoric acid can be employed under all circumstances, since its ill effects are neutralised by the complete elimination of any excess of it.

Acidulate the liquid with nitric acid, and then add excess of am-

monia. To the filtered liquid add ammonium phosphate, or simply phosphoric acid, and collect the ammonio-magnesium phosphate precipitate. To get rid of the ammoniacal salts, filter, evaporate, and calcine; this causes the greater part, or even the whole, of the hydrochloric acid to be eliminated, when that acid is present, and the two bases remain united with phosphoric acid only. However, to make certain, treat the residue two or three times with concentrated nitric acid and calcine, when the whole of the hydrochloric acid being thus eliminated, only phosphoric acid, potash, and soda remain. The residue is collected in a flask and treated by a large excess of tin and nitric acid; the phosphoric acid being thus rendered insoluble, the liquid is filtered and concentrated. The residue, composed of potassium and sodium nitrates, is calcined till completely decomposed, and as soon as the capsule is cooled the caustic alkalies are transformed into carbonates, after which they are converted into chlorides, then into sulphates, and finally ammonium carbonate is added to decompose the potassium bisulphate. With these combined elements it is possible to determine the quantity of each alkali indirectly.

The exactness of this process consists in the method of removing the phosphoric acid—a method founded on the property (discovered by A. Reynoso) possessed by stannic acid of forming a combination with phosphoric acid completely insoluble in water and in nitric acid. To render this process accurate, the hydrochloric acid must be eliminated—an object easily effected.

CHAPTER III.

CERIUM, LANTHANUM, DIDYMIUM, SAMARIUM, THORIUM, GLUCINUM, THE YTTRIUM METALS, TITANIUM, ZIRCONIUM.

CERIUM, LANTHANUM, DIDYMIUM, AND SAMARIUM.

Separation and Estimation of the Cerium Metals together.

THE precipitation of the cerium metals in the form of oxalates from a slightly acid solution is, unquestionably, the most satisfactory method of separating these oxides. The estimation of the oxalates upon a weighed filter is accompanied with the usual trouble and loss of time in perfectly drying the filter before and after collecting the precipitate upon it. By the following mode of proceeding Dr. W. Gibbs completely avoids these difficulties. The usual mixture of cerium, lanthanum, didymium, and samarium, when neutral, is to be rendered slightly acid by sulphuric or hydrochloric acid, and then largely diluted with water. Half a litre of water for every estimated gramme of oxide is a good working proportion. The solution is then to be boiled, and a hot solution of oxalic acid or ammonium oxalate added. On cooling, especially when the solution has been well stirred with a glass rod, or shaken, the oxalates separate in large crystalline grains of a pale rose-violet colour. The precipitate is to be filtered off and well washed with boiling water, the washing being extremely easy in consequence of the coarse granular character of the precipitate. The filter is then to be pierced and the oxalates carefully washed down into a crucible; after which the water in the crucible may easily be removed by evaporation, and the oxalates dried at a temperature of 100°. The equivalents of lanthanum and didymium are so near to that of cerium, that no very sensible error is committed by considering the mixed oxalates as consisting simply of cerium oxalate with three equivalents of water.

Separation of Cerium from Didymium and Lanthanum.

The following method, which we owe to the researches of Messrs. Pattison and Clarke, has been found to be very effective for the separation of cerium from didymium and lanthanum:—It is based upon the fact that when cerium chromate is evaporated to dryness and heated to about 110°, it is decomposed, and the cerium oxide remains as an insoluble powder, whilst the didymium and lanthanum chromates, when subjected to the same treatment, remain unchanged.

The mixed cerium, didymium, and lanthanum oxides are subjected to the action of an aqueous solution of chromic acid, aided by heat till solution is complete. The chromic acid need not be entirely free from sulphuric acid. The solution obtained is evaporated to dryness, and the residue heated to about 110° . Hot water is then added, which dissolves the lanthanum and didymium chromates and leaves the cerium oxide, which is then separated by filtering. Thus obtained, the cerium oxide is a yellowish-white powder which is almost completely insoluble in acids, but is rendered soluble by fusion with the acid potassium sulphate.

This process may also be employed for the quantitative determination of cerium, as it has been found, by careful trial, that not a trace of cerium can be detected by the best known processes in the solution, after its separation as above described.

Dr. Wolcott Gibbs has found that when a mixed cerium, lanthanum, and didymium salt is boiled with dilute nitric acid, and lead peroxide added to the solution, the cerium is quickly, and under some circumstances completely, oxidised, the solution becoming more or less deeply orange-yellow. This process affords an extremely simple and delicate test for cerium; it succeeds with all the salts which are soluble in nitric acid, though, of course, when the mixed oxalates are tested the oxalic acid is oxidised to carbonic acid before the characteristic cerium yellow appears. For the purpose of testing it is sufficient to dissolve the salt to be examined in nitric acid diluted with its own volume of water, to add a small quantity of pure lead peroxide and boil for a few minutes, when the smallest trace of cerium can be detected by the yellow colour of the solution. When a solution containing a cerium salt dissolved in strong nitric acid is boiled for a short time with a large excess of lead peroxide oxygen gas is copiously evolved, and, at the same time, the cerium sesquioxide formed at first is completely reduced to protoxide, the solution becoming perfectly colourless. The remarkable reaction which occurs in this case appears to be connected with the formation of lead nitrate, since, when the solution of cerium protoxide contains a large excess of this salt, the cerium is not peroxidised by boiling with nitric acid and the peroxide.

When a solution of cerium, didymium, and lanthanum is treated with nitric acid and lead peroxide in the manner pointed out above, the deep orange-coloured liquid evaporated to dryness, and heated for a short time to a temperature sufficiently high to expel a portion of the acid, it will be found that boiling water acidulated with nitric acid dissolves only the lanthanum and didymium salts, leaving the whole of the cerium in the form of basic nitrate insoluble in water. The insoluble matter is to be filtered off and thoroughly washed. A current of sulphuretted hydrogen passed into the filtrate removes the lead, after which the lanthanum and didymium may be precipitated together as oxalates, which, if the process has been carefully

performed, are perfectly free from cerium. The mass on the filter is readily dissolved by fuming nitric acid. Sulphuretted hydrogen is then to be passed through the solution, sufficiently diluted with water, until the lead is completely precipitated. The cerium may then be thrown down by oxalic acid, ignited, and weighed as ceroso-ceric oxide or converted into sulphate and weighed as such.

Cerium proto-nitrate obtained by this process gives, when tested by the spectroscope with transmitted light, even in very thick layers, a scarcely perceptible indication of didymium.

Another very good method of separating the cerium from lanthanum and didymium is to precipitate the three metals in the state of gelatinous hydrates by adding an excess of caustic potash to their solution. These oxides are washed several times by decantation, and then a concentrated solution of caustic potash added, and the whole submitted to a current of chlorine. The alkaline liquid being thus saturated with chlorine, the lanthanum and didymium oxides are redissolved, lemon-coloured insoluble ceric oxide remaining. This substance is washed on a filter, then redissolved, while still moist, in hydrochloric acid, precipitated by ammonium oxalate, and strongly calcined; the cerous oxalate is thus transformed into very light rose-coloured ceroso-ceric oxide.

The chlorinated liquid contains lanthanum and didymium oxides, which may be precipitated together by adding ammonium oxalate.

For the separation of cerium from didymium and lanthanum, as in cerite, M. H. Debray melts the mixed nitrates with 8 or 10 parts potassium nitrate in a porcelain capsule, and the fused mass is kept between 800° and 850° by means of a gas furnace. Cerium nitrate is decomposed, forming a yellowish powder of cerium oxide, which retains a little nitric acid, but didymium and lanthanum nitrates, when melted with nitre, are not appreciably decomposed, even at 850° . A thermometer, plunged into the bath of nitrate, indicates its temperature. When the escape of nitrous fumes ceases, which requires several hours, the operation is stopped. When cold the melted mass is easily detached from the capsule, and the cerium oxide is found collected at the lower part. It is dissolved in water, and there remains a powder, yellowish if it contains mere traces of didymium, but reddish if it contains more. It is well to wash with a little weak nitric acid, which dissolves a little didymium subnitrate, produced at the same time as the cerium oxide if the capsule is too strongly heated at certain points. This is of little consequence, as the cerium oxide obtained in the first operation always requires to be purified.

It may be entirely freed from didymium by transforming it into nitrate, which is melted a second time with 8 or 10 parts potassium nitrate. For this purpose the oxide is attacked with sulphuric acid diluted with an equal volume of water, when everything dissolves if the liquid is sufficiently acid. The yellow ceroso-ceric sulphate

thus obtained is reduced with sulphurous acid, and the cerous sulphate is precipitated with oxalic acid. The cerous oxalate is then readily converted into nitrate by boiling with nitric acid. This second treatment gives a yellow powder, which contains neither didymium nor lanthanum, as the nitrate of the latter earth is still more stable than that of didymium. If it is transformed into colourless cerous sulphate the spectroscope does not detect the least trace of this body, which is always easy to recognise by its absorption-spectrum. The didymium and lanthanum nitrates, which remain mixed with a large excess of potassium nitrate, are evaporated and remelted, the temperature being between 850° and 450° . The remaining trace of cerium nitrate which has escaped decomposition in the former operation is completely destroyed, and there is even formed a small quantity of didymium subnitrate. But the bulk of the didymium remains with the lanthanum in the state of a soluble nitrate.

We have thus a certain and rapid method of obtaining cerium oxide free from didymium and lanthanum, or, on the other hand, a mixture of these two oxides absolutely free from cerium.

Separation of Lanthanum and Didymium.

The nitric acid solution of lanthanum and didymium is evaporated to dryness in a flat-bottomed capsule. The dried mass is of a pale rose tint. By exposing the capsule for a few minutes to a temperature of 400° or 500° , the saline mass will be fused, with disengagement of nitrous vapours. The capsule is withdrawn from the fire before the decomposition is complete, and hot water must be poured in. Lanthanum nitrate dissolves and didymium subnitrate remains insoluble in the form of greyish-white flakes. The whole is left to stand for a few hours, then boiled and filtered; if the liquid still retains a feeble rose tint, the same operation must be repeated until a colourless liquid is obtained, containing lanthanum nitrate, free from didymium subnitrate. Lanthanum oxide is obtained by evaporating this liquid and strongly calcining the residue. The didymium oxide may also be estimated after the calcination of the subnitrate thus obtained.

This process, which was first devised by MM. Damour and Deville, is founded on the fact that didymium nitrate decomposes before lanthanum nitrate, and that the first of these salts changes to the state of subnitrate. Several precautions must be observed. The bottom of the capsule containing the mixture of the two salts must not be too much heated, nor must too large quantities of material be used, as in that case it forms a thick layer at the bottom of the capsule and decomposes unequally. It is better to recommence the operation several times than to heat too strongly in attempting to separate the two oxides at the same time. The first portions of didymium oxide obtained in this way give, with sulphuric acid, reddish-violet crystals, with

traces of white needle-shaped ones, which belong to the lanthanum sulphate. The last portions give a sulphate less coloured, but, like the preceding, with the same crystalline form derived from the oblique rhomboidal prisms; the needles of lanthanum sulphate are rather more numerous. Finally, the above-described colourless solution gives, with sulphuric acid, colourless crystals derived from the right rhomboidal prism, characteristic of lanthanum sulphate.

By following this method, the estimation of didymium comes out rather too high, and, consequently, that of lanthanum rather too low.

Dr. C. Winckler has ascertained that when cerium is separated from its solutions by mercury binoxide and potassium permanganate the cerium is not merely precipitated in the state of a peroxide, but is accompanied by didymium, whilst the lanthanum remains in solution. This is an excellent method for separating didymium from lanthanum. To obtain the didymium which accompanies the cerium in its precipitation by potassium permanganate redissolve the precipitate in hydrochloric acid. After having well calcined it to free it from the oxide of mercury, evaporate the hydrochloric solution to dryness in the presence of sulphuric acid; dissolve the residue of sulphate in water, and add potassium sulphate to it. In twenty-four hours a triple cerium, didymium, and potassium sulphate separates, insoluble in potassium sulphate.

The precipitate must then be dissolved in water, and the sulphates changed to oxalates, which are calcined to obtain the cerium and didymium oxides; these are then separated in the usual way.

The lanthanum in the filtered liquid may be obtained thus:—First treat the filtered liquid with sulphuretted hydrogen, to separate the mercury oxide, then precipitate the lanthanum as an oxalate, and calcine it. The lanthanum oxide then contains very little didymium.

Lanthanum and didymium may also be separated by taking advantage of the different solubilities of their sulphates. By digesting a mixture of the dry salts in cold water (5°), a saturated solution may be obtained, which, upon being heated to 80° deposits lanthanum sulphate, whilst didymium sulphate remains dissolved. The salts may be obtained quite pure by repeating this operation two or three times. Lanthanum sulphate is colourless, whilst didymium sulphate is of a beautiful rose-red.

Volumetric Determination of Cerium.—Franz Stolba determines ceric oxalate volumetrically by means of potassic permanganate. Pure ceric sulphate, carefully dehydrated, was dissolved to the volume of a litre, and measured portions of the solution were precipitated with ammonium oxalate, the latter being determined in the known manner with standard permanganate, the solution of the latter being standardised by means of lead oxalate.

On the other hand, portions of the solution were taken for determination as cerium oxide. Using the atomic weight $Ce=141.27$,

the quantity of cerous oxide was ascertained from the quantities of standard permanganate consumed.

The results are concordant, and where differences appeared they fall within the inevitable errors of observation. Hence, cerium, when freed from lanthanum and didymium, and separated as oxalate, may be conveniently and accurately determined as such. A corresponding quantity of sulphuric acid must be applied in titration and warm water used. During the process, the quantity of undissolved matter diminishes, and the change of colour at the conclusion is distinctly marked.

Analysis of Cerite. Separation of Cerium, Didymium, Samarium, and Lanthanum.—The mineral cerite is a hydrated cerium silicate with lanthanum, didymium, samarium, and iron; traces of some of the other rare earths are also present, as yttria, terbia, &c. As quantitative methods of any exactness for the separation of some of these earths are not yet known, the true composition of the mineral is only known approximately, and in its structure it is anything but homogeneous. Its composition agrees with the formula for the ortho-silicates, $R_2SiO_4 + aq.$, and it contains from 55 to 60 per cent. of cerium oxide, about 8 per cent. of the lanthanum, didymium, and samarium oxides, 20 per cent. of silica, and 6 per cent. of water.

To disintegrate the mineral it is finely ground, made into a thick paste with strong sulphuric acid, and heated to drive off excess of acid. The mass becomes of a white or pale grey colour. This is digested in cold water, filtered, and the residue well washed with cold water. It should be remembered that the sulphates of the cerium earths are much less soluble in hot than in cold water.

To the filtrate oxalic acid is added, which precipitates all the earths, with any lime and bismuth that may be present, as oxalates. It is sometimes advisable to ignite the oxalates so obtained and boil the residue in dilute nitric acid, by which means the didymium, samarium, and lanthanum oxides are dissolved, leaving the greater part of the cerium oxide insoluble; this method is objectionable, however, as the cerium oxide retains obstinately much didymium, and probably also lanthanum and samarium. A better plan is to heat the dried oxalates with strong nitric acid till all dissolves, and allow to cool, or dilute, when a mixture of oxalates separates out rich in didymium and samarium, the solution containing much cerium and lanthanum oxalates. For the general method of separating the earths, however, it is well to proceed as follows:—The dried oxalates are boiled with strong nitric acid till completely decomposed, evaporated to dryness, and fused at the lowest temperature at which nitrous fumes come off, the residue digested in water, filtered, and washed. The insoluble residue, of a pale yellow colour, consists of cerium oxide and basic cerium nitrate, with a little didymium, whilst the filtrate contains the lanthanum, didymium, and samarium. The operation of fusing

must be repeated on the filtrate many times to throw out all the cerium, whilst the cerium oxide, or basic nitrate obtained, is freed from any didymium by retreatment with nitric acid and fusion as above; the presence of didymium in it being indicated by its brown colour or by the absorption spectrum of the solution. To free the didymium, &c., nitrates from the last traces of cerium it is necessary to fuse them with three or four times their weight of potassium nitrate, very gently, at a temperature just sufficient to cause slight decomposition.

The separation of lanthanum, didymium, and samarium from each other is a most laborious process, and the amounts of these earths, obtainable in anything like a pure state, small, compared with the mass of material worked up. The solution of the nitrates of these elements is made perfectly neutral, diluted to such a strength as to contain about 1 per cent. of the oxides and a very dilute solution of ammonia added, about .1 gramme NH_3 in 500 cubic centimetres; the precipitation being conducted in large vessels, such as ordinary Winchester quart bottles. The first precipitates formed are rich in samarium but containing much didymium; these are followed by didymium, with some lanthanum and samarium; and the final precipitates consist almost wholly of lanthanum. By this method there is obtained three portions of hydrates, which must be again worked up separately by precipitation as above; the first for samarium, the second for didymium, and the third for lanthanum, the process of fractional precipitation being repeated on each portion fifty or a hundred times.

The separation of the last traces of didymium from the samarium can only be accomplished by fractional precipitation, an operation so tedious that few chemists will probably be inclined to undertake it. The second portion of hydrates, consisting chiefly of didymium, is purified from the small quantities of samarium and lanthanum it contains by fusing with potassic nitrate for the samarium, as explained above for the traces of cerium; whilst to separate the lanthanum the oxalates are dissolved in warm strong nitric acid and allowed to cool, when didymium oxalate nearly free from lanthanum is obtained; repeated several times, the last trace of lanthanum remains in the solution.

To separate the small quantity of didymium from the lanthanum obtained as the final precipitate with ammonia, the only method is by a continuation of the process of fractionation; the lanthanum oxide finally obtained should be pure white, any trace of a yellowish tinge indicating didymium still present.

As cerite contains small quantities of the yttria earths, these may be separated from cerium, didymium, &c., by making a cold solution of the sulphate and adding finely-powdered potassium sulphate in quantity more than sufficient to saturate the solution, allowed to stand (with frequent agitations) for a few days and filtered; washing the filtrate with a saturated solution of potassium sulphate. The filtrate contains the yttria earths, and for their complete separation it is

advisable to repeat the operation with potassium sulphate three or four times. The insoluble residue, consisting of a double sulphate of potassium, cerium, didymium, &c., is boiled with sodium hydrate, filtered, well washed, redissolved in nitric acid, precipitated with oxalic acid, and the oxalates ignited, leaving the earths—lanthana of a pure white colour, didymia of a deep chocolate brown, and samaria of a pale brown colour.

Separation of Thorium from other Earthy Metals.

Prof. L. Smith has discovered an exact method for separating thoria from the other earths. It consists, like the method employed for separating cerium from didymium and lanthanum, in suspending the oxides recently precipitated in water containing four to five times their weight of caustic potash or soda and in passing a current of chlorine into the liquid. All the oxides are dissolved, save those of cerium and thorium, the residue being a gelatinous precipitate, like alumina. He has also employed fractional precipitation with ammonia for separating the greater part of the thoria in operations on a large scale; the thoria comes down first, but the separation is not sufficiently exact for analytical purposes.

GLUCINUM.

Preparation of Pure Glucina.

The simplest way to prepare a chemically pure glucinum salt is to make use of the process devised by Dr. W. Gibbs. The crude glucina obtained in the ordinary manner from beryl, but still contaminated with alumina, iron, &c., is fused with twice its weight of acid potassium fluoride, and the fused mass treated with boiling water, to which a small quantity of hydrofluoric acid has been added. On filtering, a notable quantity of the insoluble aluminium and potassium fluoride almost always remains upon the filter, even when the separation of glucina has been carefully executed by means of ammonium carbonate. The filtrate, on cooling, deposits colourless transparent crusts of the double glucinum and potassium fluoride, which are easily purified by recrystallisation.

Glucina may be prepared direct from beryl by this process, but as beryl only contains 18 or 14 per cent. of glucinum, it will be more economical to separate the other oxides, as far as possible, by the ordinary methods, and then to purify the crude glucina by the above process.

From the aqueous solution of the double fluoride, pure glucina may be precipitated directly by ammonia.

Separation of Glucinum from the Cerium Metals.

The separation may best be effected in the following way:—Convert

the salts into sulphates, and dissolve in the smallest quantity of water. If iron be present, reduce it to the state of protosulphate, by passing a stream of sulphuretted hydrogen through the hot solution; if this precaution is not taken, the precipitated double sulphates will contain iron. Then add a saturated solution of sodium sulphate (which Dr. W. Gibbs has shown to be greatly superior to potassium sulphate for this purpose), and sufficient of dry sodium sulphate in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sulphates of sodium and the cerium metals separate immediately as a white, highly crystalline powder, which is thrown upon a filter and washed thoroughly with a hot saturated solution of sodium sulphate. After washing, the double sulphates on the filter are to be dissolved in hot dilute hydrochloric acid, the solution largely diluted with water, and the cerium metals precipitated by ammonium oxalate. From the filtrate the glucinum may be precipitated at once by ammonium hydrate.

THE YTTRIUM METALS.

Analysis of the Natural Tantalates containing the Yttrium Metals.—Prof. J. L. Smith calls attention to the use made for their solution of concentrated hydrofluoric acid, whose action, especially upon the samarskite and euxenite of North Carolina, is as rapid and energetic as that of hydrochloric acid upon calcareous spar. If finely-powdered samarskite is taken, moistened with its own weight of water, and treated with twice its weight of fuming commercial hydrofluoric acid, the attack takes place in the cold in a few seconds, the mass heats with a slight effervescence, and the decomposition is effected in from five to ten minutes. If needful, the action may be assisted by exposure to the heat of the water-bath for a few moments. The capsule is then kept at the temperature of boiling water long enough to expel the excess of acid. The contents of the capsule are then treated with 80 to 40 grammes of water (to 5 grammes of mineral) thrown upon a filter and carefully washed, adding, if needful, one or two drops of hydrofluoric acid. The mineral is thus separated into two portions—the filtrate, containing all the metallic acids and the iron and manganese oxides, and the insoluble precipitate, containing all the earths and uranic oxide. The difficulty of the attack increases with the proportion of tantalic acid in the minerals. The most interesting constituents of samarskite are the earths. In the description already published of the North Carolina variety, the author merely arranged the earths in two classes—the yttria group and the cerium group—remarking that the latter probably did not contain cerium oxide, and that the thorina detected in the variety from the Urals was present in too small quantity to be recognised in a satisfactory manner. He has

since found that the earths of the yttria group consist of about two-thirds yttria and one-third erbia.

Separation of the Yttrium Metals from Glucinum.

These metals may be separated by mixing the precipitated hydrated oxides with sugar, drying, and then heating to redness in a covered crucible. The black carbonised mass is then introduced into a piece of combustion-tubing, and heated to redness, whilst a slow current of dry chlorine is passed over. The chlorides of the yttrium metals are non-volatile, whilst glucinum chloride volatilises and may be collected in any appropriate condenser.

Separation of the Yttrium Metals from those of Cerium.

The yttrium metals behave the same as glucinum, in respect to sodium sulphate. The double sulphates of sodium and the yttrium metals, being readily soluble in sodium sulphate solution, may be separated from cerium, lanthanum, and didymium in the way detailed on page 68.

ON THE DETECTION AND WIDE DISTRIBUTION OF YTTRIUM.¹

Introduction.

1. 'In March, 1881, I sent to the Royal Society a preliminary notice of some results I had obtained when working on the molecular discharge in high vacua.² When the spark from a good induction coil traverses a tube having a flat aluminium pole at each end, the appearance changes according to the degree of exhaustion. Supposing atmospheric air to be the gas under exhaustion, at a pressure of about 7 millimetres a narrow black space is seen to separate the luminous glow and the aluminium pole connected with the negative pole of the induction coil. As the exhaustion proceeds this dark space increases in thickness, until, at a pressure of about 0.02 millimetre (between 20 and 80 M.),³ the dark spark has swollen out till it nearly fills the tube. The luminous cloud showing the presence of residual gas has almost disappeared, and the molecular discharge from the negative pole begins to excite phosphorescence on the glass where it strikes the side. There is a great difference in the degree of exhaustion at which various substances begin to phosphoresce. Some refuse to glow until the exhaustion is so great that the vacuum is nearly non-conducting, whilst others begin to become luminous when the gauge is 5 or 10 millimetres below the barometric level. The majority of bodies, however, do not

¹ 'The Bakerian Lecture, by William Crookes, F.R.S. Delivered before the Royal Society, May 31, 1883.

² 'Proceedings of the Royal Society, No. 213, 1881.

³ 'M = one-millionth of an atmosphere.

phosphoresce till they are well within the negative dark space. This phosphorogenic phenomenon is at its maximum at about 1 M., and, unless otherwise stated, the experiments now about to be described were all tried at this high degree of exhaustion.

‘Under the influence of this discharge, which I have ventured to call radiant matter, a large number of substances emit phosphorescent light, some faintly and others with great intensity. On examining the emitted light in the spectroscope most bodies give a faint continuous spectrum, with a more or less decided concentration in one part of the spectrum, the superficial colour of the phosphorescing substance being governed by this preponderating emission in one or other part of the spectrum.

‘Sometimes, but more rarely, the spectrum of the phosphorescent light is discontinuous, and it is to bodies manifesting this phenomenon that my attention has been specially directed for some years past, considerable interest attaching to a solid body whose molecules vibrate in a few directions only, giving rise to spectrum lines or bands on a dark background.

‘The Citron-Band Spectrum.

2. ‘For a long time past I have been haunted by a bright citron-coloured band or line appearing in these phosphorescent spectra, sometimes as a sharp line, at others as a broader nebulous band, but having always a characteristic appearance and occurring uniformly in the same spot. This band I first saw in the summer of 1879, and from that date down to a comparatively short time ago all my efforts to clear up the mystery proved vain. By chemical means it was not difficult to effect a partial separation of a certain mineral or earthy body into two parts, one giving little or no citron band, the other giving one stronger than the original band; and by again treating this latter portion by appropriate chemical means, the citron band-forming body could frequently be still more concentrated; but further than this for a long time it seemed impossible to go. I soon came to the conclusion that the substance I was in search of was an earth, but on attempting to determine its chemical properties I was baffled. A more Proteus-like substance a chemist never had to deal with. In my preliminary note, above referred to, speaking of the possibility that some of these spectrum-forming bodies might be new chemical elements, I said: “The chemist must be on his guard against certain pitfalls which catch the unwary. I allude to the profound modification which the presence of fluorine, phosphorus, boron, &c., causes in the chemical reactions of many elements, and to the interfering action of a large quantity of one body on the chemical properties of another which may be present in small quantities.”

3. ‘This warning was not unnecessary. No Will-o’-the-Wisp ever led the unwary traveller into so many pitfalls and sloughs of despond

as the hunt for this phantom band has entrapped me. I have started with a large quantity of substance which, from preliminary observations, promised to be a rich mine of the desired body, and have worked it up chemically to a certain point, when the citron band vanished, and could not be again detected in either precipitate or filtrate. Half-a-dozen times in the last four years the research has been given up as hopeless, and only a feeling of humiliation at the thought of a chemist being beaten by any number of anomalies made me renew each time the attack. Likewise, the tedious character of the research made a long continuance of failures very disheartening. To perform a spectrum test, the body under examination must be put in a tube and exhausted to a very high point before the spectroscopie can be brought to bear on it. Instead of a few minutes, many hours are occupied in each operation, and the tentative gropings in the dark, pre-eminently characteristic of this kind of research, have to be extended over a long period of time.

4. 'I soon found that the best way to bring out the band was to treat the substance under examination with strong sulphuric acid, drive off excess of acid by heat, and finally to raise the temperature to dull redness (10). The anhydrous sulphate thus left frequently showed the citron band in the radiant matter tube, when before this treatment the original substance showed nothing (75).

'Examination of Calcium Compounds.

5. 'My first idea was that the band might be due to a compound of lime. Much chemical evidence tended to support this view. I have already explained that the chemical extraction was rendered very difficult by the fact of the citron band so frequently turning up both in the precipitate and the filtrate. By neglecting the portion showing the least citron band, and separating all the elements present which gave little or none, I could generally concentrate the citron band into a solution which—according to our present knowledge of analytical chemistry—should contain little else than the earths, alkaline earths, and alkalis. Ammonia added to this solution would precipitate an earth (11, 14), and in the filtrate oxalic acid would precipitate an insoluble oxalate (7, 18).

'The citron band hovered between these two precipitates, being sometimes stronger in one and sometimes in the other. It was also to be detected, but more faintly, in the residue left after evaporating to dryness and igniting the filtrate from the oxalate.

'I frequently obtained no precipitate with ammonia, and then the oxalate gave the band brilliantly; and occasionally the ammonia precipitate when formed gave little or no citron band. I was, however, generally sure to find it in the insoluble oxalate, and sometimes it was very brilliant, being accompanied by two bright green bands and a fainter red band.

6. ' At this time one of the minerals which showed the citron band most strongly was a phosphorescent apatite from Ireland ; and knowing the difficulties of separating the last traces of phosphoric acid from the earths, I explained the foregoing facts by the presence of small quantities of phosphoric acid, which gave rise to the ammonia precipitate; the bulk of the citron body not being precipitated by ammonia, but coming down as oxalate ; whilst a little of this oxalate would remain dissolved in the ammoniacal salts present, and so appear with the alkalis.

' I tested this hypothesis in every imaginable way, by mixing small quantities of phosphoric acid with salts of lime and other earths, in the endeavour to imitate the conditions occurring in the native minerals, and so educe the citron band ; but I was unable to get any precipitate giving the citron band when I started with materials which did not originally give it.

7. ' A sufficient quantity of precipitated oxalate (5) having in course of time been accumulated, I attempted its purification. It was ignited, dissolved in dilute hydrochloric acid, and rendered slightly alkaline with ammonia and ammonium sulphide. The liquid was boiled to a small bulk, keeping it alkaline, and was then set aside in a warm place : a slight flocculent precipitate formed. This was filtered, and the filtrate reconcentrated. The clear strong solution should now contain nothing but barium, strontium, and calcium, with traces of elements from previous groups which might be soluble in the precipitants employed or in the ammoniacal salts present (for we know that the word *insoluble* applied to a precipitate is not an absolute term, and in minute analysis allowance must be made not only for the slight solubility of precipitates in the reagents present, but also for the power possessed by most precipitates of carrying down with them traces of soluble metallic salts from solution). Besides these, it was possible that a hitherto unrecognised element might be present, to which the citron band was due. By the ordinary process of analysis I could, however, only detect the presence of calcium and strontium.

8. ' The concentrated ammoniacal solution was added to an excess of a boiling solution of ammonium sulphate, and the whole was set aside for twenty-four hours ; the precipitate which had formed was filtered off and washed with a saturated solution of ammonium sulphate. The precipitate was found to consist of strontium sulphate. On testing this in a radiant matter tube the citron band was very decided, although much fainter than in the original oxalate. The filtrate was diluted largely, heated, and precipitated with a hot solution of ammonium oxalate ; it was then allowed to stand for some time, when a bulky white calcium oxalate came down. This was filtered and washed. Tested in the radiant matter tube, after ignition and treatment with sulphuric acid, it gave the citron band, far exceeding in brightness the spectrum of the original oxalate.

9. 'So far all the chemical evidence went to show that the band-forming substance was calcium, and further tests tried with the purified oxalate confirmed this inference. Every analytical test to which it was subjected showed lime, and nothing but lime; all the salts which were prepared from it resembled those of lime, both physically and chemically; the flame spectrum gave the calcium lines with extraordinary purity and brilliancy; and finally, the atomic weight, taken with great care, came out almost the same as that of calcium, 89.9 as against Ca 40.

10. 'I now sought for the citron band amongst other calcium minerals. The preliminary testing was simple. The finely-powdered mineral was moistened with strong sulphuric acid, the action being assisted by heat, and the mass was raised to dull redness (4). It was then put into a radiant matter tube and the induction spark passed through after the exhaustion had been pushed to the required degree.

'Treated in this manner most native compounds of lime gave the citron band. A perfectly clear and colourless crystal of Iceland spar converted into sulphate gave it strongly, native calcic phosphate less strongly, and a crystal of arragonite much more brightly. A stalactite of calcium carbonate from the Gibraltar caves gave the band almost as well as calcite, as also did cinnamon stone (lime alumina garnet), iron slag from a blast-furnace, commercial plaster of Paris, and most specimens of ordinary burnt lime.

'The Citron Band not due to Calcium.

11. 'Evidence stronger than this in favour of the view that the citron band was an inherent characteristic of calcium could scarcely be; but, on the other hand, there was evidence equally conclusive that the band was not essential to calcium. The ammonia precipitate (5) sometimes gave the citron band with great strength and purity, and although I had not yet obtained this in quantities sufficient for a detailed examination, it was easy to decide that it contained no phosphoric, silicic, or boric acid, fluorine, or other body likely to cause the precipitation of lime in this group. This precipitate must therefore be an earth, and the more carefully I purified it from lime and other substances, the more brilliantly shone out the citron band, and the more intense became the green and red bands.

'Another stubborn fact was this:—Starting with a lime compound which showed the citron band, I could always obtain a calcium oxalate which gave the band stronger than the original substance; but if I started with a lime compound which originally gave no citron band, I could never by any means, chemical or physical, constrain the lime or the earthy precipitate to yield a citron band.

12. 'Among the minerals tried was eudialyte, a zirconium, iron, calcium, and sodium silicate, containing about 10 per cent. of lime.

No citron band could be detected on testing the original mineral or any of the constituents separated from it on analysis. This and a lump of common whiting (levigated chalk) were for some time my only sources of lime which gave no citron band.

13. 'The only explanation that I could see for this anomaly was that the elusive citron band was caused by some element precipitated with the calcic oxalate, but present in a quantity too small to be detected by ordinary chemical means. I then thought that were I to fractionally precipitate the solution of lime, the band-forming body might be concentrated in one or the other portion. Accordingly the calcium oxalate (7, 8, 9) was ignited and dissolved in hydrochloric acid, and fractionally precipitated in three portions with ammonium oxalate, the first and third portions being comparatively small. They were dried, ignited with sulphuric acid, and tested in the radiant matter tube. All three portions showed the citron band, but the portion which came down first gave the band decidedly the strongest, and the third portion precipitated showed it weakest. This therefore pointed to a difference between calcium and the body sought for. The process, however, was not satisfactory, and I was driven to seek some other method.

14. 'A portion of an ammonia precipitate found to give the citron band very well (5, 11) was dissolved in dilute sulphuric acid, and the solution evaporated down. Crystals were formed which were difficultly soluble in hot water, but appeared more soluble than calcic sulphate.

'A large quantity of the calcic oxalate (7, 8, 9) was ignited with sulphuric acid at a dull red heat, and the resulting calcium sulphate was finely ground and then boiled in a very small quantity of water—not sufficient to dissolve the one-hundredth part of it. The mass was thrown on a filter, and the small quantity of clear liquid which came through was precipitated with ammonium oxalate. The resulting white precipitate was ignited with sulphuric acid, and tested in the radiant matter tube. For the sake of comparison a portion of the calcium sulphate remaining on the filter was also put in a radiant matter tube. The sulphate from the aqueous extract gave the citron band far more brilliantly than the calcium sulphate from the filter. I found, however, that it was impossible, by any amount of washing or boiling out, to deprive the calcium sulphate of all power of giving the citron band, although it was possible in this way to weaken its intensity considerably.

'Experiments with Calcium Sulphate.

15. 'Supposing that the substance giving the citron band formed a sulphate more soluble in water than calcium sulphate, it was anticipated that repeated washings with cold water would extract some of it, which might then be detected more easily. About 4 lbs. weight of commercial plaster of Paris, which showed very faint traces of the citron band, were mixed with water and rapidly poured on a

large filter. Before the mass solidified a slight saucerlike depression was made in the upper part, and a few ounces of water were poured on. This ran through slowly, and it was then poured back and the exhaustion repeated several times. The aqueous extract was then evaporated to dryness, ignited with sulphuric acid, ground in a mortar with small successive quantities of water, the liquid boiled, filtered, and precipitated first with ammonia, and the filtrate with ammonium oxalate. These precipitates both showed the citron band very fairly, far more intensely than it was seen in the original calcium sulphate. The green and red bands were also visible.

'The same mass of plaster of Paris was then washed, as before, with a little dilute hydrochloric acid passed through several times, and this extract was treated in the same way by evaporation and extraction with water, and the filtrate precipitated, first with ammonia, and then with ammonium oxalate. In these precipitates the citron band, together with the green and red bands, were much more brightly manifest than in the precipitates from the aqueous extract.

'Wide Distribution of the Citron Band-forming Body.

16. 'These experiments are conclusive in proving that the citron band is not due to calcium, but to some other element, probably one of the earthy metals, occurring in very minute quantities, but widely distributed along with calcium, and I at once commenced experiments to find a more abundant supply of the body sought for. Amongst other substances tested I may note the following as giving a more or less decided citron band in the spectrum when treated with sulphuric acid in the manner indicated above (10):—Crystallised barium chlorate, heavy spar, common limestone, strontium nitrate, native strontium carbonate, crystallised uranium nitrate, commercial magnesium sulphate, commercial potassium sulphate, Wagnerite (magnesium phosphate and fluoride), zircon, cerite, and commercial cerium oxalate.

'Examination of Zircon for the Citron Band.

17. 'Some specimens of zircon treated in the above manner appeared sufficiently rich to make it probable that here might be found an available source of the citron band-yielding body. I found it in crystals from Green River, North Carolina, from Ceylon, from Espailly, from Miask (Oural), and from Brevig, and having a good supply of North Carolina zircons I started working up these in the following manner:—

'The finely-powdered zircons were fused with sodium fluoride, and the melted mass powdered, boiled with sulphuric acid, and filtered. The solution was precipitated with excess of ammonia, the precipitate well washed and dissolved in hydrochloric acid, and the solution made nearly neutral. A little zirconium oxychloride sometimes separated on evaporation; this was filtered off. An excess of sodium thiosulphate

was now added, and the whole boiled for some time until a portion of the filtrate gave no further precipitate on boiling again with sodic thio-sulphate. The precipitated zirconium thiosulphate was worked up for zirconia; it was found to be quite free from the substance giving the citron band. The solution filtered from the zirconium thiosulphate was precipitated with ammonia, and the brown gelatinous precipitate was well washed. The filtrate was precipitated with ammonium oxalate, which brought down much calcium oxalate. This showed the citron band, but not strongly. The brown gelatinous precipitate was dissolved in nitric acid. Silver nitrate was added to separate chlorine, and the filtrate from the silver chloride was boiled down with nitric acid and excess of metallic tin to separate phosphoric acid. The clear solution, separated from the stannic oxide, phosphate, &c., was boiled down with hydrochloric acid to remove nitric acid, and then saturated with hydric sulphide to separate silver and tin.

18. 'The filtrate from the sulphides was freed from hydric sulphide by boiling, and was then mixed with tartaric acid and excess of ammonia, to precipitate any yttria that might be present, together with Forbes' zirconia β^1 (jargonite?). On standing for some hours this gave a small quantity of a precipitate, which was separated by filtration; it was tested in the radiant matter tube, and found not to give the citron-band spectrum (44). To the filtrate ammonium sulphide was added to precipitate the iron. The black precipitate was filtered off and the filtrate evaporated to dryness, and ignited to destroy the organic matter. The residue, heated with sulphuric acid and ignited, gave the citron spectrum very brightly. This would probably be the earth which Forbes calls zirconia γ .²

19. 'For many years chemists have suspected that what is known as zirconia might be a compound. Svanberg³ found that zircons from different localities varied in specific gravity, and the earth or earths obtained by fractional precipitation with oxalic acid had not the same properties, the hydrogen equivalents of the metals of the earths of the different fractions varying from 17.01 to 27.8, the metal of the earth hitherto recognised as zirconia being 22.4.⁴ He considered zirconia to contain two different earths, the oxalate of one being less soluble in acid than that of the other, and their sulphates differing in crystalline form and solubility. He proposed the name "noria" for one of the earths, retaining that of zirconia for the other. The researches of Berlin, on the other hand, seem to disprove this.

¹ P. 98, and 'Chemical News, vol. xix. p. 277.

² P. 98, and 'Loc. cit.

³ 'Poggend. Annal. vol. lxx. p. 317.

⁴ 'Svanberg's numbers for these earths are 938 to 1820 (M_2O_3), the earth hitherto recognised as zirconia being 1140; oxygen being 100. For the sake of uniformity I have recalculated his equivalents for the metals on the O = 16 scale, taking the formula as M_2O (see note 1, par. 40).

20. 'Remembering the remarkable result produced in the absorption spectrum of some jargons by the presence of a minute trace of uranium,¹ I tried numerous experiments with this metal, adding small quantities of it to zirconia, lime, thoria, ceria, &c., but in no case could I educe the citron-band spectrum by this means.

'I may condense a year's work on zircon—more than 10 lbs. weight of crystals from North Carolina having been worked up—by stating that the result was comprised in about 800 grains of an earthy residue (18), and about two ounces of oxalate, chiefly calcium; the former gave the citron band very well. The process as detailed above is given, since by this means a very large quantity of zircons was worked up, affording me the material which ultimately enabled me to solve the problem, which at one time seemed almost hopeless.

'The zirconia prepared from these zircons when tested sometimes showed the citron band, especially after precipitation as an oxychloride. Zirconia precipitated as thiosulphate did not yield the citron band (28.) A zirconia rich in citron band, fractionally precipitated by ammonia, yielded precipitates of increasing richness, the last fraction showing the citron band strongly.

21. 'The calcium oxalate obtained from zircon gave unsatisfactory results, so attention was directed to the earthy residue (18). This was found to be of highly complex character, containing thoria (which had escaped precipitation as thiosulphate), ceria, lanthana, didymia, yttria, and probably some of the newly-discovered rarer earths.

'Examination of Cerite for the Citron Band.

22. 'The position of the citron band in the spectrum falls exactly on the strongest absorption band of didymium, so that a piece of didymium glass or cell of solution of the nitrate entirely obliterates the citron band. This naturally suggested that the band was due to didymium.

'Cerite was accordingly the next mineral experimented on. The powdered mineral tested in the tube in the original way gave a good citron band. It was made into a paste with sulphuric acid, and after all action had ceased it was extracted with cold water. The earths were then precipitated with ammonium oxalate, and the oxalate ignited. The fawn-coloured powder was then converted into sulphate, dissolved in water, and the cerium metals precipitated by long digestion with excess of potassium sulphate. When no didymium bands could be detected in a considerable thickness of the supernatant liquor it was assumed that all the cerium metals were down, and the liquid was filtered.

23. 'The precipitated double sulphates were dissolved in hydrochloric acid, and the earths precipitated as oxalates. After ignition and treatment with sulphuric acid, the mixed ceria, lanthana, and

¹ 'Chemical News, vol. xix. pp. 121, 142, 205, 277; vol. xx. pp. 7, 104; vol. xxi. p. 73.

didymia were tested in the radiant matter tube, but the merest trace only of citron band was visible.

24. 'This experiment proved the inadequacy of the didymium explanation (22), and further tests showed that not only could I get no citron band in pure didymium compounds, but the spectrum entirely failed to detect didymium in many solutions of the earth which gave the citron band brilliantly.

25. 'Attention was now turned to the solution filtered from the insoluble double sulphates from cerite (22). Potash in excess was added to the filtrate, and the flocculent precipitate was filtered off, and after well washing was converted into sulphate, and tested in a radiant matter tube. The spectrum, of extraordinary brilliancy, was far brighter than any I had hitherto obtained. Unfortunately, however, the quantity was too small to be subjected to very searching chemical analysis.

'Examination of Thorite and Orangite.

26. 'Search was next made amongst other minerals rich in the rarer earths. Thorite, another disputed mineral, was finely powdered, treated with sulphuric acid, and tested in the radiant matter tube. It gave the citron spectrum most brilliantly—equal, in fact, to the mixture of earths obtained from zircons (18, 21) at so great an expenditure of time and trouble. Orangite treated in the same manner gave almost as good a spectrum. Pure thorium sulphate prepared by myself was found not to give the citron band, but three specimens prepared and given to me by friends all gave it, so it was not unlikely that in thorite and orangite might at last be found a good source of the long-sought element—that in fact the body I was hunting for, if not thorium, might possibly be Bahr's hypothetical wasium. Having obtained about 2 lbs. of orangite and thorite, they were worked up as follows:—

27. 'The finely-powdered mineral was heated for some time with strong hydrochloric acid, and when fully gelatinised and all action had ceased, it was evaporated to dryness to render the silica insoluble; then extracted with water slightly acidulated with hydrochloric acid, boiled, and filtered. Hydric sulphide was passed through the filtrate for some time. The flask then corked was set aside for twenty-four hours and filtered. The filtrate was evaporated to a small bulk, nearly neutralised with ammonia, and then boiled for some time with excess of sodium thiosulphate. This precipitated the thorium, alumina, zirconia, and titanous acid, whilst it left in solution the metals of the cerium and yttrium groups. The filtrate was boiled down to a small bulk, when a further precipitation took place: this was filtered off and added to the first thiosulphate precipitate. To the clear filtrate excess of ammonium oxalate was added, and the whole allowed to rest twenty-four hours. The precipitated oxalates were filtered, washed, ignited, dissolved in hydrochloric acid, and the excess of acid evaporated off. The aqueous solution was then mixed with a large excess of freshly precipitated

barium carbonate, and set aside for twenty-four hours with frequent shaking (29). This would precipitate much of the cerium, and any iron or alumina which might have escaped previous treatment. The liquid was filtered from the precipitate by barium carbonate, and the clear solution, which would contain nothing but barium, and some of the yttrium and cerium metals, was treated as described farther on (30).

28. 'The thiosulphate precipitate tested in the radiant matter tube gave no citron band, nor did it seem possible to detect this band on testing the purified thoria obtained from this precipitate, nor from the alumina or zirconia from the same precipitate. This confirmed the results obtained when working up zircons, that sodium thiosulphate did not precipitate the citron band-forming body.

29. 'The barium precipitate (27) was dissolved in hydrochloric acid, the baryta separated with sulphuric acid, and the solution precipitated with ammonium oxalate. The ignited precipitate, which amounted to 0.228 per cent. of the mineral taken, contained the cerium metals. On testing in a radiant matter tube it gave the citron band only moderately well—not nearly so strong as the original thorite and orangite. The iron and alumina in the filtrate from the cerium oxalates were likewise precipitated and tested; they showed a faint trace of citron band.

30. 'The solution (27) filtered from the barium precipitate was freed from baryta by sulphuric acid, precipitated with ammonium oxalate, and the precipitate washed and ignited; it amounted to only 0.125 of the mineral taken. Tested in the radiant matter tube it showed the citron band about as well as the corresponding earth from the barium precipitate.

'This was disheartening, for after having started with a mineral which gave the citron band well, and having hunted the citron band as it were into a corner, the only result was two trifling precipitates showing the citron band less intensely than did the raw material itself. The experiment, however, proved one thing: the band-forming substance was not thoria. The occurrence of this spectrum must therefore be due to some other element present in small quantity in thorite and orangite.

31. 'The two mixtures of earth—the one from the barium precipitate (29) and the other from the barium filtrate (30)—which showed the citron line moderately well, were dissolved in sulphuric acid, the solution neutralised as nearly as possible with potash, and digested for several days with excess of potassium sulphate. The solution, which at first showed the didymium bands, was then found to be free from didymium.

32. 'The insoluble double sulphates were filtered and washed with a cold saturated solution of potassium sulphate. The precipitate was boiled for some time in ammonia, filtered, dissolved in hydrochloric acid, and precipitated with ammonium oxalate. This precipitate was ignited and tested in the radiant matter tube. It gave scarcely a trace

of citron band (28). The earth was further purified by the potash and chlorine method, and was found to consist principally of cerium oxide.

33. 'The solution filtered from the insoluble potassio-cerium sulphate (31) was boiled with ammonia and ammonium sulphide. A small quantity of a white flocculent earth came down—too small a quantity to weigh. Tested in a radiant matter tube, it gave the citron band better than either of the above precipitates, showing that by this treatment the body had been concentrated (25).

34. 'It seemed possible that the earth sought for might be present in larger quantity in the thorite, but that it had been gradually carried down mechanically or by mass-action rather than chemically, by the numerous operations it had undergone before getting it to the final stage. Therefore a fresh quantity of thorite was extracted with hydrochloric acid. The solution was precipitated with potassium sulphate, taking the usual precautions to secure complete precipitation. A bulky precipitate ensued, which contained the thorium and cerium earths. These were separated and tested, and found to give only a faint citron band.

35. 'The solution of earthy sulphates soluble in potassium sulphate was precipitated with ammonium oxalate. The precipitate ignited with sulphuric acid, and tested in a radiant matter tube, gave the citron spectrum with great brilliancy (25, 33).

' Chemical Facts connected with the Citron Body.

36. 'Certain chemical facts concerning the behaviour of the sought-for element which came out during the course of the tentative trials already described had considerably narrowed the list amongst which it might probably be found. All the evidence tended to show that it belongs to the group of earthy metals, consisting of aluminium, glucinum, thorium, zirconium, cerium, lanthanum, didymium, and the yttrium family, together with titanium, tantalum, and niobium. The sought-for earth is insoluble in excess of potash (25); this excludes aluminium and glucinum. It is not precipitated by continued boiling with sodium thiosulphate (17, 27); this excludes aluminium, thorium, and zirconium. Fused with acid potassium sulphate, the resulting compound is readily soluble in cold water; this excludes tantalum and niobium. Evaporating to dryness with hydrochloric acid and heating for some time does not render the mass insoluble in water (27); this excludes titanium and silicium. It is easily soluble in an excess of a saturated solution of potassium sulphate (25, 33, 34); this excludes thorium, the cerium group, some of the numerous members of the yttrium group, and zirconium. The only remaining elements among which this elusive body would probably be found are those members of the yttrium family which are not precipitated by potassium sulphate.

87. 'On the other hand, the body giving the citron-band spectrum did not behave like one of the known earths. A rich residue was fused with sodium carbonate, and the mass extracted with water. The insoluble residue, on testing in the usual way, was rich in citron band, but subsequent treatment of the aqueous solution gave me an earth which also gave the citron band strongly.

'An acid solution of the citron body was precipitated by ammonia and ammonium chloride. The earth was not completely precipitated, but after a long boiling some remained in solution. I have since ascertained that the detection of the citron band body in solution under these circumstances is only owing to the marvellous delicacy of the test, which carries our powers of recognition far beyond the resources of ordinary chemistry.

88. 'Besides obtaining indirect evidence that the citron-band was not due to certain elements, I tried special experiments with each substance, brought to the highest possible state of purity. In many cases I detected more or less traces of citron band; but I had come to the conclusion, abundantly warranted by facts, that this citron band was an extraordinarily sensitive test of the presence of the element causing it; and the minute chemistry of many of these earthy metals being insufficiently known, it was not surprising that traces of one of them should adhere to another in spite of repeated attempts to purify it out. With each successive fractional precipitation the citron band became fainter, showing that with perseverance the last trace would probably disappear. The time this process would have occupied, in my opinion, seemed not worth the little additional evidence it would have afforded.

89. 'Taking into consideration the extremely small quantity of phosphorescent material which had so far been obtained, all these experiments justified me in assuming that the body sought for not only belonged to the group of earths, but also most probably to the subgroup, not precipitated by potassium sulphate, to which yttria belongs. As, however, the number of these metals has increased so much within the last few years, and as the quantity of material which I had up to the present at my disposal was too small to admit of a satisfactory chemical examination being made of it, search was commenced among other sources known to be rich in these metals. Besides, not only did the majority of the substances I had up till now obtained in anything like quantity indicate the citron-band earth to belong to the yttria group (83, 84, 86), but also that either the earth itself showed an absorption band in the spectroscope, or was invariably accompanied by one which did. On the other hand, I had a certain amount of evidence that the earth sought for did not show a band in the spectroscope (24); but remembering the extremely small quantity of very impure substance experimented with, the evidence on this point was not at all conclusive.

‘The Sought-for Body one of the Yttrium Family.

40. ‘The yttria earths form a somewhat numerous family. Fortunately for chemists, a mineral rich in yttria earths—samarските—has been found in large quantity in Mitchell County, North Carolina, and to this mineral I accordingly now directed my attention.

‘The annexed list of elements of the yttrium and its allied families, said to occur in samarskite and similar minerals, may be considered complete to the present time.

Name.	Absorption Spec-trum.	Hydrogen equivalent of Metal. ¹ (Type of Oxide M ₂ O.)	Name.	Absorption Spec-trum.	Hydrogen equivalent of Metal. ¹ (Type of Oxide M ₂ O.)
Cerium . .	No	47.1 ²	Samarium . .	Yes	50.0 ¹⁴
Columbium ³ . .	Yes	—	Scandium . .	No	14.7 ¹⁵
Decipium . .	Yes	57.0 ⁴	Terbium . .	No	49.5 ¹⁶
Didymium . .	Yes	48.5 ⁵	Thorium . .	No	58.4
Didymium β . .	Yes	47.0 ⁶	Thulium . .	Yes	56.5 ¹⁷
Erbium . .	Yes	55.3 ⁷	Ytterbium . .	No	57.9 ¹⁸
Holmium ⁸ . .	Yes	54.0 ⁹	Yttrium . .	No	29.7 ¹⁹
Lanthanum . .	No	46.0 ¹⁰	Yttrium α . .	No	52.2 ²⁰
Mosandrum . .	No	51.2 ¹¹	Yttrium β . .	Yes	49.7 ²¹
Philippium ¹² . .	No	—	Zirconium . .	No	22.5
Rogierium ¹³ . .	Yes	—			

¹ As it is at present doubtful whether the oxides of several of the metals in this table belong to the type M₂O, M₂O₃, or MO, I have, for the sake of uniformity and simplicity, in calculating the values from the composition of their salts, by which these metals are chiefly discriminated, taken the type of oxide to be M₂O.

² Bührig, *J. Pr. Chem.* ser. 2, vol. xii. p. 209.

³ Dr. J. Lawrence Smith, in a paper read before the United States National Academy of Sciences in 1879, announced the discovery in samarskite of two new elements, which he named Columbium and Rogerium (*Nature*, vol. xxi. p. 146). I have failed to find any further notice of these elements. This columbium must not be confounded with the well-known columbium, sometimes called tantalum.

⁴ Delafontaine, *Comptes Rendus*, vol. lxxxvii. p. 632, vol. xciii. p. 63; *Chemical News*, vol. xxxviii. p. 223, vol. xlv. p. 67.

⁵ Clève, *Bull. Soc. Chim.* ser. 2, vol. xxi. p. 246. Brauner, *Comptes Rendus*, vol. xciv. p. 1718; *Chemical News*, xlvii. p. 175.

⁶ Clève, *Comptes Rendus*, vol. xciv. p. 1528; *Chemical News*, vol. xiv. p. 273. Brauner, *Comptes Rendus*, xciv. p. 1718; *Chemical News*, vol. xlv. p. 16.

⁷ Clève, *Comptes Rendus*, vol. xci. p. 381; *Chemical News*, vol. xlii. p. 199. Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxix. p. 516; *Chemical News*, vol. xl. p. 147.

⁸ Called by Soret, the first discoverer, X. Subsequently Clève discovered the same metal and called it holmium. Soret has now adopted Clève's name. *Comptes Rendus*, vol. lxxxix. p. 708, and vol. xci. p. 378; *Chemical News*, vol. xl. p. 224; and vol. xlii. p. 199. Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxix. p. 516; *Chemical News*, vol. xl. p. 147.

⁹ Clève, *Comptes Rendus*, vol. lxxxix. p. 478; *Chemical News*, vol. xl. p. 125.

41. 'Some of these claimants will certainly not stand the test of further scrutiny. Thus samarium and yttrium β are in all probability identical; and I should scarcely have included philippium, as Roscoe¹ has conclusively proved that this is a mixture of terbium and yttrium, and my own results (61) confirm those of Roscoe. Moreover, others of these so-called elements will probably turn out to be mixtures of known elements. But in the confessedly very imperfect state of our knowledge of the chemistry of these metals it is not safe for me in this research to assume that any one of them will surely not survive. The complete list as it stands will therefore be taken to contain all hitherto claimed as new, although it is almost certain to include too many.

'The Sought-for Body has no Absorption Spectrum.

42. 'In the second column "Yes" or "No" indicates whether the solutions give an absorption spectrum when examined by transmitted

¹⁰ 'Brauner, *Comptes Rendus*, vol. xciv. p. 1718; *Chemical News*, vol. xlv. p. 16.

¹¹ 'Lawrence Smith, *Comptes Rendus*, vol. lxxxvii. pp. 145, 146, 148. Marignac, *ibid.* vol. lxxxvii. p. 281. Delafontaine, in October, 1878 (*ibid.* vol. lxxxvii. p. 600), considers mosandrum a mixture of terbium, yttrium, erbium, didymium, and philippium. Subsequently, however, Lawrence Smith, in November, 1878 (*ibid.* vol. lxxxvii. p. 881), adduces chemical and other reasons to show that his mosandrum is not a mixture, but a true element. A year later, September 1, 1879 (*ibid.* vol. lxxxix. p. 480), Lawrence Smith repeats the claim for mosandrum to be classed with the elements.

¹² 'Delafontaine, *Comptes Rendus*, vol. lxxxvii. p. 559; *Chemical News*, vol. xxxviii. p. 202; *Journ. Chem. Soc.* vol. xxxvi. p. 116.

¹³ 'See note 3 to columbium, *ante*.

¹⁴ 'Lecoq de Boisbaudran, *Comptes Rendus*, vol. lxxxviii. p. 322, and vol. lxxxix. p. 212; *Chemical News*, vol. xxxix. p. 115, and vol. xl. p. 99. Brauner, *Chemical News*, vol. xlvii. p. 175; Clève, *Comptes Rendus*, vol. xcvi. p. 94; *Chemical News*, vol. xlviii. p. 39.

¹⁵ 'Nilson, *Comptes Rendus*, vol. xci. p. 118; *Chemical News*, vol. xlii. p. 83. Clève, *Comptes Rendus*, vol. lxxxix. p. 419; *Chemical News*, vol. xl. p. 159.

¹⁶ 'Marignac, *Ann. Chim. et Phys.* ser. 5, vol. xiv. p. 247; *Journ. Chem. Soc.*, vol. xxxvi. p. 118. Delafontaine, *Ann. Chim. et Phys.* ser. 5, vol. xiv. p. 238; *Journ. Chem. Soc.* vol. xxxvi. p. 114.

¹⁷ 'Clève, *Comptes Rendus*, vol. lxxxix. p. 478, and vol. xci. p. 328; *Chemical News*, vol. xl. p. 125, and vol. xlii. p. 182. Thalen, *Comptes Rendus*, vol. xci. p. 376; *Chemical News*, vol. xlii. p. 197.

¹⁸ 'Marignac, *Comptes Rendus*, vol. lxxxvii. p. 578; *Chemical News*, vol. xxxviii. p. 213. Nilson, *Comptes Rendus*, vol. lxxxviii. p. 642, vol. xci. p. 56; *Chemical News*, vol. xlii. p. 61.

¹⁹ 'Clève, *Comptes Rendus*, vol. xcvi. p. 1225; *Chemical News*, vol. xlvii. p. 4; *Bull. Soc. Chim.* vol. xxxix. p. 120; *Chemical News*, vol. xlvii. p. 143.

²⁰ 'Marignac, *Comptes Rendus*, vol. xc. p. 899; *Chemical News*, vol. xli. p. 250.

²¹ 'This is almost certainly identical with Lecoq de Boisbaudran's samarium. See Marignac, *Comptes Rendus*, vol. xc. p. 899; *Chemical News*, vol. xli. p. 250. Soret, *Comptes Rendus*, vol. xci. p. 378; *Chemical News*, vol. xlii. p. 199.

¹ ' *Journ. Chem. Soc.* vol. xli. p. 277.

light. Now, could I definitely settle whether solutions of the citron-band body gave an absorption spectrum or not, I could at once eliminate a whole class of elements.

'This was not difficult to determine. I have already said (22, 24) that spectroscopic examination entirely failed to detect didymium in many solutions of the earth which gave the citron band strongly. This was not always the case. In early days of this research I frequently obtained absorption bands innumerable when the citron-band body was known to be present; but as I became better acquainted with the chemical reactions of the new earth I gradually succeeded in eliminating one after the other those metals yielding absorption spectra. The earth from zircons (18, 21) gave the most satisfactory results in this respect. This, after removing the little didymium present, gave but a trace of an absorption spectrum, which from its general appearance was probably due to erbia. The earth obtained from cerite (25), which gave the citron spectrum with great brilliancy, on the other hand yielded no absorption spectrum; and generally I may say that, whenever I started with a sufficient quantity of an earth giving both citron-band spectrum and absorption spectrum, I could, by appropriate chemical means, always separate it into three portions,—one which gave the citron-band spectrum with great brilliancy, and showed in concentrated solution a very faint absorption spectrum, and frequently none at all; another which gave very little citron-band spectrum, but a good absorption spectrum; and a third intermediate portion—about four-fifths of the whole—which gave both citron-band and absorption spectrum. This portion, by repetition of the treatment, could again be split up in the same way, and the operation repeated as often as the stock of the material held out.

43. 'Having definitely settled the question that the metal giving the citron-band spectrum was not one of those giving an absorption spectrum, the possible elements become materially narrowed to the following list:—Cerium, lanthanum, mosandrum, scandium, terbium, thorium, ytterbium, yttrium, yttrium α , and zirconium.

'Of these the potassium sulphate reaction (86) excludes cerium, lanthanum, scandium, thorium, yttrium α , and zirconium, so there are left only the following:—

Mosandrum,
Ytterbium,

Terbium,
Yttrium.

44. 'Certain chemical reactions for a long time made me dismiss yttrium from the list of likely bodies. In my analysis of zircons (18), towards the latter part of the process, I used the following process to separate the iron:—The solution, mixed with tartaric acid and excess of ammonia, was allowed to stand for some time. A small quantity of a precipitate gradually formed, which was filtered off, and it was this filtrate, after separating the iron with ammonium sulphide, that yielded the greatest quantity of substance giving the citron-band. Now one

of the methods of separating yttria from alumina, glucina, thoria, and zirconia is to precipitate it as tartrate in the presence of excess of ammonia, the other earths remaining in solution. Fresenius says: "The precipitation ensues only after some time, but it is complete."

'The precipitate thus obtained with tartaric acid and ammonia should therefore contain all the yttria: *it gave no citron-band whatever in the radiant matter tube*; whilst the residue, which should be free from yttria (18), proved for a long time the only source of material wherewith to investigate the chemical properties of the body giving the citron spectrum.

45. 'Another reason which made me, at this stage of the research, pass over yttria, was that I had already tested this earth in the radiant matter tube. In a paper on "Discontinuous Phosphorescent Spectra in High Vacua," read before the Royal Society, May 19, 1881,¹ I said, "Yttria shows a dull greenish light giving a continuous spectrum" (75).

'For these reasons I for a long time omitted yttria from my list of possible bodies, and considered that the earth, if not a new one, might turn out to be either mosandra, terbia, or ytterbia.

'Analysis of Samarskite.

46. 'A very large quantity (about 15 lbs. weight altogether) of samarskite was worked up, partly by the hydrofluoric acid method of Lawrence Smith,² and partly by fusion with potassium bisulphate. The niobic and tantalic acids after purification were found to give no citronband spectrum.

'These methods both gave as a result a large quantity of mixed earths containing most, if not all, of the bodies enumerated in par. 40. Tested in the radiant matter tube, this material gave the citron spectrum very brilliantly. It was dissolved in hydrochloric acid, neutralised as nearly as possible with ammonia, and boiled with sodium thiosulphate. This precipitated the thoria, zirconia, and alumina. In this precipitate some of the scandia might also be found if present in quantity, but as scandium thiosulphate is not completely precipitated, and the earth is present only in minute traces, not much scandia, it is probable, was thus carried down.

'This thiosulphate precipitate, treated in the usual way with sulphuric acid, gave no citron band in the radiant matter tube.

47. 'The filtrate from the thiosulphate was precipitated hot with excess of ammonia, and the precipitate after washing treated with sulphuric acid, dried, and heated till fumes of sulphuric acid disappeared. The sulphate, whitish with a very pale rose tint, was finely ground,

¹ 'Proc. Roy. Soc. No. 213, 1881.

² 'Comptes Rendus, vol. lxxvii. p. 146.

and dissolved with frequent agitation in the smallest possible quantity of cold water—an operation which required much time. The solution was then precipitated with potassium sulphate, taking all necessary precautions to keep the liquid well saturated with potassium sulphate. This operation was allowed to go on for about ten days, when the precipitated double sulphates were filtered off and slightly washed with a saturated solution of potassium sulphate. The precipitate contained cerium, lanthanum, didymium, didymium β , decipium, samarium, scandium, yttrium α , yttrium β , together with any thorium and zirconium which might have escaped the thiosulphate treatment.

48. 'The filtrate from the double sulphates was precipitated hot with ammonia, which brought down the erbia, holmia, mosandra, terbia, thulia, ytterbia, and yttria. The small quantity of manganese in solution was in this operation completely thrown out.

49. 'The insoluble double sulphates (45) were dissolved in hydrochloric acid, precipitated hot with ammonia, washed till free from potassium salts, redissolved, precipitated as oxalates, ignited, and set aside for further examination. On testing in the radiant matter tube this mixture of oxides was found to be practically free from citron band.

50. 'The ammonia precipitate from the sulphates soluble in potassium sulphate (46) was well washed till free from potassium salts, and dissolved in excess of nitric acid. The concentrated solution gave an absorption spectrum showing lines belonging to erbium and allied metals. Having already proved that the body I was seeking was not one of those metals which gave an absorption spectrum (42, 43), my first object was to find some method by which I could roughly separate this mixture of earths into two portions, one giving absorption bands, and the other having no action on the transmitted spectrum. I found this was possible by taking advantage of the different solubility of the oxalates in nitric acid.

51. 'The highly acid solution of the nitrates was fractionally precipitated in the following manner:—

'To the boiling liquid a solution of ammonium oxalate was added drop by drop. The precipitate at first formed redissolved on stirring. The cautious addition of ammonium oxalate was repeated until the precipitate refused to dissolve entirely, but left the hot liquid somewhat milky. It was then rapidly cooled with constant stirring, which brought down a heavy crystalline oxalate. This was filtered off, and called oxalate A. The filtrate, again heated to boiling, was precipitated in exactly the same way with a further quantity of ammonium oxalate till the hot liquid became opalescent. On cooling and stirring, a further quantity of oxalate came down. The filtrations and precipitations were repeated until no more precipitate could be obtained. Usually I could get twelve or thirteen fractionations in this manner; towards the end the solution did not get milky, and it had to stand sometimes twenty-four hours before much oxalate came down.

52. 'The fractions first precipitated by oxalic acid gave very strong absorption bands when the concentrated solutions of the oxides were examined by transmitted light. The fractions last precipitated showed the absorption bands only faintly.

53. 'These operations gave me oxalates from A to L. These, ignited, with free access of air, were then each dissolved in nitric acid, and again separately fractionated as oxalates. The result was about 150 precipitates, ranging from $A_1 A_2 \dots A_{12}$, $B_1 B_2 \dots B_{12}$, to $L_1 L_2 \dots L_{12}$.

'These, after ignition, were separated into five lots according to order of colour, and the fractionation of each of the five lots repeated as already described; the series of operations now closely resembling those of Pattinson's process for desilvering lead. This gave me about sixty lots. This time the hydrogen equivalent of the metal of each lot was taken by converting the oxalate into sulphate and estimating the sulphuric acid, assuming M_2O to be the type of oxide (40, note 1). The result was a series of earths having hydrogen equivalents (M) ranging from about 48 to 93. The earths were now sorted into high, low, and intermediate, those giving intermediate H equivalents being refractionated with repeated H equivalent estimation, the highest and lowest being each time separated and added to the former high and low lots.

54. 'The ultimate result of about five hundred fractional precipitations gave me a mixture of earths having an H equivalent $M=48$, and showing a strong absorption spectrum (56); a mixture having an H equivalent $M=83$, having no absorption spectrum (65); and intermediate earths.

'In the radiant matter tube all these fractions gave the citron-band spectrum well, but that of the earth of lowest equivalent was much the brightest, and that of the highest equivalent the least intense.

55. 'Three methods are available for the partial separation of these earths and for the complete purification of any one of them. The formic acid process (56, 57) is best for separating terbia, as terbic formate is difficultly soluble in water, the other formates being easily soluble.

'Fractional precipitation with oxalic acid (63, 64, 65) separates first erbia, holmia, and thulia, then terbia, and lastly yttria. This is the only method which is applicable for the separation of small quantities of terbia from yttria.

'Fusing the nitrates (60, 68, 69) separates ytterbia, erbia, holmia, and thulia from yttria. It is not so applicable when terbia is present, and is most useful in purifying the gadolinite earths. This process is the only one known for separating ytterbia from yttria.

'Selection must be made of these methods according to the mixture of earths under treatment, changing the method as one earth or the other becomes concentrated on one side or thrown out on the other.

Each operation must be repeated many times before even approximate purity is attained. The operations are more analogous to the separation of members of homologous series of hydrocarbons by fractional distillation than to the separations in mineral chemistry as ordinarily adopted in the laboratory.

'Preparations of Pure Terbia.

56. 'The mixture of high equivalent earths (54) richest in terbia, erbia, holmia, and thulia was treated as follows:—

'The earths were dissolved in dilute formic acid, and the solution heated for some time. A white powder of terbium formate separated. This was filtered off, the solution containing the more easily soluble formates evaporated to dryness, and ignited. In this way the $M = 48$ earths were separated into two lots, one rich in terbia and the other rich in erbia, &c. The treatment with formic acid was again repeated on both lots, and the crude terbia finally purified as follows:—

57. 'The crude terbia from all the operations was systematically treated by the formic acid process, keeping the liquid so dilute that only a portion of the terbium formate separated out each time. The syrupy solution of formates was treated as described further on (60). The hydrogen equivalent of the terbium was taken each time; latterly it kept pretty constant at 49.5. The terbia was also tested in the radiant matter tube. At first the citron spectrum was very strong; gradually, however, it got fainter and fainter under the repeated formic treatment, until finally the spectrum became so weak as to satisfy me that it was due only to impurity in the terbia, and that, had the material been sufficient to stand against the extravagant process of purification adopted, I should finally have got a terbia giving no citron-band spectrum. (Subsequent examination (87) showed me that this terbia did not contain more than $\frac{1}{8000}$ part of yttria.)

58. 'A concentrated solution of the purest terbia obtained in this way, when examined by the spectroscope, showed no absorption lines whatever: proving the absence of erbium, holmium, and thulium.

59. 'The hydrogen equivalent (49.5) would not definitely show the absence of ytterbium (57.9) and yttrium (29.7); but these would have been separated by the formic acid treatment, terbium formate requiring 30 parts of water for its solution, whilst yttrium and ytterbium formates dissolve in less than their own weight of water. Moreover, it was not probable that the terbia contained an appreciable quantity of any of these earths as an impurity, for neither the oxalic acid, the fusing nitrate, nor the formic acid process of fractionation produced any change in the atomic weight, 49.5.

Preparation of Mixed Erbium, Holmium, and Thulium, free from other Earths.

60. ' The filtrate from the terbium formate (57), rich in erbium, and containing besides terbium, holmium, thulium, and yttrium, was now treated by converting it into nitrates, evaporating to dryness, and submitting the mass to careful fusion, stopping the operation when the liquid mass began to evolve nitrous fumes. The erbium, holmium, and thulium nitrates decomposing before the yttrium nitrate, extraction with water gave an insoluble residue rich in erbium, holmium, and thulium, and a filtrate rich in yttrium. The insoluble residue was dissolved in nitric acid, again evaporated to dryness, and fused. These operations were repeated eight or ten times, with the result of raising the H equivalent of the erbium metals to about 56.8, but the citron-band spectrum remained strong for some time after. It, however, ultimately disappeared. A concentrated solution of this erbium, &c. nitrate showed a beautiful and intense absorption spectrum. I did not attempt any separation of erbium, holmium, and thulium from each other, as the evidence here obtained is sufficient to show that the element giving the citron-band spectrum is not one of these three metals. Likewise I had far too little material to enable me to enter on a work of such difficulty with any prospect of success.

' Philippia.

61. ' The so-called philippia was sought for in the portion of earths intermediate between the terbium and yttrium (54). These were dissolved in dilute formic acid, and the solution, filtered from some terbium formate which would not dissolve, was carefully evaporated down to a small bulk, filtering off the terbium or other difficultly soluble formates as they deposited. The clear concentrated solution was then set aside over sulphuric acid to crystallise. In the course of a few days brilliant rhombic prisms crystallised out, having exactly the appearance described by Delafontaine.¹ The finest of these crystals were picked out, dried on blotting-paper, and analysed. The hydrogen equivalent was found to be $M=38.2$. The citron-band spectrum in the radiant matter tube was very brilliant. The solution decanted from these crystals was evaporated to a syrupy consistency, filtered from insoluble terbium formate which deposited, and treated for yttrium (65).

' Some of the best rhombic crystals were added to cold water acidulated with formic acid, and gently heated, but all attempts to dissolve and recrystallise them failed. A large quantity of an insoluble formate separated, and the mother-liquor on concentration again deposited shining rhomboidal crystals. On attempting to recrystallise these, they again deposited an insoluble white powder. The mother-liquor

¹ ' *Comptes Rendus*, vol. lxxxvii. p. 599; *Chemical News*, vol. xxxviii. p. 202; *Journ. Chem. Soc.* vol. xxxvi. p. 116.

was found to contain a large quantity of yttria, and the white insoluble formate on ignition gave an earth having the atomic weight and chemical behaviour of terbia. This entirely corroborates Professor Roscoe's conclusions,¹ that Delafontaine's philippia is nothing but a mixture of yttria and terbia.

' Mosandra.

62. ' The chemical characters of this earth are so little known that I could not attempt to search for it. But as the citron-band-forming earth always appeared concentrated amongst those whose double sulphates were most soluble in potassium sulphate,—and, of these, amongst those having the palest colour and lowest atomic weight,—it was scarcely conceivable that the earth I was in search of should ultimately prove to be one whose properties did not in any case correspond to these,—of a dark orange-yellow colour, forming a difficultly soluble double potassium sulphate, and having the very high equivalent of $M=51.2$: these being the properties ascribed to mosandra by the discoverer, Professor Lawrence Smith.

' Separation of Terbia and Yttria from Erbia, Holmia, and Thulia.

63. ' The mother-liquors, from which as much terbium formate as possible had been separated by the process above described (56, 57) were now evaporated down with nitric acid till all the formates were decomposed, and the highly acid solutions of nitrates were fractionally precipitated with oxalic acid (51, 52, 53).

64. ' The erbium, holmium, and thulium oxalates come down first; then the terbium oxalate; lastly, the yttrium oxalate (53). After repeated fractional precipitations I at last succeeded in obtaining a mixture of yttria and terbia of a golden colour, which gave a very brilliant phosphorescent spectrum in the radiant matter tube, but showed no trace of absorption band when the concentrated solution of the nitrates was examined in the spectroscope.

' Separation of Terbia and Yttria.

65. ' The crude yttria was now added to the mixture of earths (54) having a hydrogen equivalent to $M=33$, and the whole submitted again to fractionation with oxalic acid in a somewhat modified manner.

' An excess of strong nitric acid was added to the solution of mixed terbium and yttrium nitrates, and the solution was heated to the boiling-point. Strong oxalic acid solution was added drop by drop till a faint permanent precipitate was produced. Strong nitric acid was now added, a drop at a time, till the solution again became clear, and the whole was allowed to cool very slowly without agitation. On cooling, an oxalate crystallised out in brilliant prisms. These contained nearly

¹ ' *Journ. Chem. Soc.* vol. xli. p. 277.

all the terbia with some of the yttria, whilst the mother-liquor contained most of the yttria with a little terbia. The filtrate was treated with more oxalic acid, a fresh crop of crystals being produced, when the crystals were ignited, and the resulting earths re-treated with nitric acid and oxalic acid. After repeated fractionations I finally obtained in this manner a perfectly white yttria and a terbia containing a small quantity of yttria. This terbia was added to the crude terbia from previous operations, and purified as already described (57).

' These operations gave me two earths,—yttria and terbia,—which, from the constancy of their H equivalents, were taken to be pure. The earths giving absorption spectra and having H equivalents other than 29.7 and 49.5, include erbia, holmia, and thulia. This portion was not further examined for the purposes of this investigation.

' Ytterbia.

66. ' Before considering it finally proved that the substance forming the citron-band spectrum was yttria, it was necessary to prepare ytterbia and ascertain its behaviour in the radiant matter tube, this earth and yttria being the only remaining earths to which the citron spectrum could possibly belong.

' The two metals have hydrogen equivalents—ytterbium 57.9 and yttrium 29.7. The chemical reactions are also sufficiently different to render their separation a matter of no very great difficulty.

67. ' Gadolinite is said by Nilson to contain most ytterbia, so this mineral was chosen in preference to samarskite. The crude earths were first purified from all the earths whose sulphates are difficultly soluble in potassium sulphate (22, 25, 81 to 86), then by the formic acid process from terbia (56, 57), and lastly by fractional precipitation with oxalic acid from the erbia earths (65). There remained an almost white yttria, which gave the citron-band spectrum very brilliantly. Now, gadolinite contains only about 0.1 per cent. of ytterbia, and about 85 per cent. of yttria; therefore the ytterbia to yttria in this mixture was somewhat in the proportion of 1 to 300, and it gave the citron-band spectrum as brilliantly as I had ever seen it. The probability was that the earth forming nearly the whole was the one giving the spectrum.'

68. ' Ytterbium nitrate decomposes on fusion almost as easily as erbium nitrate (60), whilst yttrium nitrate resists decomposition much more energetically.¹ Fusion of the nitrates is also the best process for throwing out the erbia, holmia, and thulia, and is therefore the best for purifying gadolinite yttria, as this mineral is rich in the erbia earths and contains little terbia.

' The gadolinite yttria was converted into nitrate, fused for a short time, and extracted with water. The portions soluble and insoluble

¹ ' Marignac, *Comptes Rendus*, vol. xc. p. 902.

in water were again separately submitted to this treatment, until at last a colourless earth was obtained, the nitrate of which decomposed easily on fusion, and another whose nitrate resisted decomposition when exposed for a long time to nearly a red heat (70).

'The earth from the easily decomposed nitrate gave at first a faint citron-band spectrum, evidently due to impurity. On repeating the operation several times I at last succeeded in obtaining a white earth which gave only the merest trace of citron-band spectrum. Its hydrogen equivalent, 58.0, and its chemical properties showed that it was probably Marignac's ytterbia. Subsequent experiments satisfied me that this earth did not contain more than $\frac{1}{10000}$ part of yttria (84, 87). The extreme tediousness of the chemical operations necessary to obtain this high degree of purity, and the long time they require, prevented me from pushing these results beyond what was necessary to prove the special point at issue.

'Purification of Yttria.

69. 'The white earth obtained in the operation described at par. 65 might still contain traces of terbia, together with erbia, holmia, and thulia. I had relied on the absence of absorption spectrum as proving the absence of erbia, holmia, and thulia, but this test is not a very delicate one, and a final purification was therefore attempted. The decomposition of the fused nitrates was now the process relied on for this final purification, the yttrium nitrate resisting nearly a red heat without decomposition, whilst the erbium, holmium, and thulium nitrates are decomposed at a much lower temperature. The operation was carried on as described at par. 60.

'The yttrium nitrate left undecomposed, after repeated fusions, was now fused at a higher temperature, extracted with water, filtered from insoluble residue, and the operation repeated on the filtrate. After several such operations the H equivalent of the yttria was taken at every succeeding operation, and the spectral appearance in the radiant matter tube was also examined. The equivalent gradually got down to 81.0, but the spectra did not vary very much; that from the earth of lowest equivalent being, however, the most brilliant.

70. 'The yttrium nitrate, prepared from gadolinite and freed from ytterbia by the fusion of the nitrates (68), was converted into oxalate and ignited. The resulting yttria was quite white, and on testing in the radiant matter tube gave a spectrum absolutely identical with that given by the zircon (18), cerite (25), thorite and orangite (83, 84), and samarskite (64, 69), yttrias. Pure yttria was also prepared from yttrotantalite, euxenite, allanite, tyrite, and also from plaster of Paris (15) and common limestone. In no case could I detect any difference in the position or intensity of the lines shown by their phosphorescent spectra.



'The Phosphorescent Spectrum of Yttria.

71. 'The spectrum shown by pure ignited yttrium sulphate in a radiant matter tube is one of the most beautiful objects in the whole range of spectroscopy. The lines are not so sharp as those given by spark spectra, but are more like the flame spectra of the alkaline earths. The spectrum is best seen under low dispersion and not too narrow a slit. The accompanying cut gives an accurate map of the spectrum. I have given in line No. 1 the position of the principal Fraunhofer lines for comparison of position. Line No. 2 gives the position of the bands, and No. 3 the relative intensities represented by the heights of the ordinates. The numbers along the top refer to a scale of squared oscillation frequencies, or of the squared reciprocals of wavelengths.

72. 'Commencing at the red end, two narrow faint bands are seen at 2245 and 2275, followed by a stronger and broader red band extending between 2355 and 2415. Another faint band occurs between 2577 and 2610, followed after a very narrow black interval by a stronger reddish-orange band extending to 2627. Another faint orange band occurs at about 2800, with edges too indistinct for measurement. At about 2940 a faint yellow band appears, extending to about 3025. The strong citron-coloured band follows closely from 3028 to 3049; and a little farther on, between 3100 and 3120, a much fainter citron band is seen. Two characteristic green bands follow after a dark interval; the first, very bright, extending between 3312 and 3320, but shading off each side; the second somewhat fainter, but more sharply defined than the first, extending from 3420 to 3440; there is also a third faint green band, between 3460 and 3467. At 3780 is the centre of a narrow and faint bluish-green band; at 4110 to 4125 is a blue band; and at 4296 another blue band commences, and, extending a short distance, fades away so gradually as to render measurement of the farther side impossible. At 5052 and 5851 are two violet lines, but they are not sufficiently sharp to enable accurate measurements to be taken.

'I have carefully compared the spark spectrum given by yttrium chloride with the phosphorescent spectrum, and have not found any similarity between them, neither have I detected any discontinuity of spectrum on examining the faint light shown by yttrium compounds in Becquerel's phosphoroscope.

73. 'The above description applies to the spectrum shown either by pure yttria or by an earth tolerably rich in yttria. When traces are present the citron band only is seen. A little more yttria brings out the first and then the second green band, and finally, as the proportion of yttria increases, the red and blue bands appear (80 to 86).

'Circumstances modifying the Yttria Spectrum.

74. 'In the early days of this investigation I frequently found that an earthy mixture which by one mode of treatment gave no spectrum, would give a good citron band by a modification of the treatment, and I gradually found that I was most likely to get the spectrum when the body had been treated with sulphuric acid and then ignited to dull redness (4). Not knowing the circumstances governing the appearance of the citron band, it would not then have been safe to have altered this mode of treatment. Now, however, having ascertained the earth to which the spectrum was due, and having a considerable quantity at my disposal, experiments were tried on other methods of treating yttria before exposing it in the radiant matter tube.

75. 'Pure yttria precipitated by ammonia from the sulphate was dried at a temperature below redness and tested. It did not phosphoresce in the slightest degree, and, necessarily, no citron-band spectrum was to be seen. The yttria was removed from the tube, converted into sulphate, heated to redness, and again tested. It now gave the citron band magnificently. This shows what apparently trivial circumstances will alter the whole course of an investigation. In 1881, when searching for discontinuous phosphorescent spectra, I tried a similar experiment with pure precipitated yttria (45) and entirely missed its citron-band spectrum. Had I first treated the yttria with sulphuric acid, instead of testing the earth itself in the radiant matter tube, the results would have been very different, and this research would probably have never been undertaken.

76. 'Yttria was now prepared by igniting the precipitated oxalate at a red heat. On testing in the radiant matter tube it phosphoresced with feeble intensity, the light being about one-twentieth of that given by the ignited sulphate under similar conditions. The citron band was almost as sharp as the sodium line, and was shifted one division towards the blue end, now occupying the position 8050 to 8060, its former place 8028 to 8049 being quite dark. The appearance is shown in line No. 4. On superposing this spectrum and that from the ignited sulphate the displacement of the citron bands was clearly observed; with a very narrow slit the two bands were seen not to touch. The two green bands were visible, but very hazy and indistinct, and only to be resolved into bands with difficulty. The yttria was now removed from the tube, ignited to a bright red heat, and re-tested. The spectrum was a little stronger than that given by the yttria ignited at a lower temperature, but in other respects the general appearance and measurements were unchanged. No alteration was caused by subsequent ignition to a white heat.

77. 'Pure yttrium sulphate ignited to a bright white heat gave a

spectrum corresponding to the oxide (76); the sulphate having been decomposed by the high temperature.

78. 'Yttrium phosphate was precipitated, washed, and dried at a heat below redness, and introduced into the radiant matter tube. It phosphoresced faintly, giving the citron band hazy and faint, extending from about 8010 to 8060. The red bands were faint, and the green bands, especially the first one, were stronger than usual. The salt was now removed from the tube and heated to redness. It became of a grey colour, and now phosphoresced with a beautiful green light. The citron band was still broad and faint, but the green bands were very bright and distinct, and the red band between 2610 and 2627 was also stronger. The spectrum No. 5 shows the appearance.

'Heating the phosphate before the blowpipe made little change in the character of the phosphorescence. It was moistened with sulphuric acid, heated to a dull redness, and then tested, but no further change was produced in the spectrum. This experiment shows that the citron-band test for yttrium is far less delicate in the presence of phosphoric acid than in its absence.

'Occurrence of Yttria in Nature.

79. 'It is an old and probably a true saying that every element could be detected everywhere had we sufficiently delicate tests for it. Early observations (10, 16) had prepared me for the wide distribution of the element giving the citron band, and no sooner had the exquisite sensitiveness of this spectrum test forced itself on my notice than I sought for yttrium in other minerals. Facts which I had noticed in connection with the variation of the appearance of the citron spectrum, according to the quantity of yttrium present, showed that it might be possible to devise a process for the rough quantitative estimation of yttrium, and after several experiments this was ultimately carried out in the following manner :—

'The calcium carbonate which was found to give no citron band (12) was boiled in a quantity of nitric acid insufficient to dissolve it. The solution was filtered from the insoluble residue, diluted to a convenient bulk, and standardised : 14.91 grains of solution contained 1 grain of calcium. This operation was performed in a room in which had been no yttria compound, and the chemicals and apparatus were new, and had not been taken into the general laboratory. A portion of the standard solution was precipitated with ammonium oxalate, and the calcium oxalate ignited and treated with sulphuric acid. Tested in the radiant matter tube it gave no citron band.

'Pure yttrium sulphate was dissolved in water to such a strength that 8000 grains of solution contained 1 grain of yttrium.

80. 'The solutions were mixed together in the proportion of 1 of yttrium to 100 of calcium, evaporated to dryness, and ignited with

sulphuric acid, and the residue tested in a radiant matter tube. The spectrum was bright, the citron band, the two green bands, the blue and the red bands showed distinctly.

81. 'A mixture was now prepared in the proportion of 1 of yttrium to 500 of calcium, and tested as above. The citron band was strong, but the green bands were fainter; the blue bands were still visible.

82. 'A mixture containing 1 of yttrium to 1000 of calcium was next prepared. In the radiant matter tube the citron band was almost as strong as in the last experiment, but, the edges were not so sharp, the blue bands were faint, and the green bands had disappeared.

83. 'A mixture containing 1 of yttrium to 5000 of calcium tested in the radiant matter tube showed the citron band still very bright, but hazy about the edges. No other bands were seen.

	Parts.
Pink coral (one particular specimen)	One part of yttrium in 200
Strontianite	One " " 500
Stilbite	One " " 500
Hydrodolomite, from Vesuvius	One " " 500
Witherite	One " " 1000
Arragonite	One " " 2000
Chondrodite (Humite) from Vesuvius	One " " 4000
Egyptian syenite (Cleopatra's Needle)	One " " 7000
Calcite	One " " 10,000
Natrolite	One " " 10,000
Ox bone	One " " 10,000
Meionite (Vesuvius)	One " " 10,000
Meteorite (Alfianello, Feb. 16, 1883)	One " " 100,000
Brevicite	One " " 200,000
Prehnite	One " " 500,000
Thomsonite	One " " 500,000
Vesbine, mixed with lava, from Vesuvius	One " " 700,000
Dolomite	One " " 1,000,000
Tobacco ash	One " " 1,000,000
Leucite, from Vesuvius	Less than one " 1,000,000
Nepheline, from Vesuvius	None
Meteorite (Dhumsala, 1860)	None
Analcite	None
Phenakite	None
Chrysolite	None
Hätynite	None
Turquoise	None

84. 'A mixture of 1 yttrium and 10,000 of calcium was now tried. The citron band was still decided, but not at all sharp.

85. 'One of yttrium to 100,000 of calcium was next prepared and tested. The citron band was faint, but easily seen. It could not, however, be obtained at all sharp, and appeared broader than usual.

86. 'A mixture of 1 of yttrium and 1,000,000 of calcium was lastly prepared, and tested in the radiant matter tube. The citron band was very faint, but there was no mistaking its presence, and with care I have no doubt a smaller quantity than 1 in 1,000,000 could be detected. This, however, appears to be near the limit of the test.

87. 'These seven tubes were mounted on a board, so that connection with the induction coil could rapidly be made to either of them; and various minerals, &c., were prepared and tested in radiant matter tubes (10). By comparing their spectra with those of the standard tubes I could, after a little practice, determine roughly the proportion of yttrium present, supposing the test not to be interfered with by the presence of phosphoric acid (78).

88. 'In the table given on the preceding page are some of the most interesting results obtained in this way.'

TITANIUM.

Detection and Estimation of Titanium.

Mr. B. Apjohn proceeds as follows:—Twelve grammes of the finely-powdered rock are fluxed with six times their weight of acid potassium sulphate, and the heat is continued until the greater part of the free sulphuric acid is driven off. The cooled mass is reduced to a fine powder, exhausted with cold water, and the aqueous solution, largely diluted, boiled with acid sodium sulphate. As soon as the precipitation is complete, the contents of the flask are allowed to cool, and a little sulphurous acid is added to redissolve any iron or aluminium which might have been precipitated. This precipitate of titanic acid is converted into the potassium titano-fluoride in the usual manner, and the salt thus obtained is collected on a weighed filter, washed with a few drops of cold water, dried, and weighed; and from this weight the amount of titanic acid is reduced.

For the detection of small quantities of titanium, especially when mixed with iron, alumina, and silica, E. Jackson adds hydrogen peroxide to the acid (hydrochloric or nitric) solution. A fine yellow or orange colour appears. Ferric chloride should not be present. An excess of hydrofluoric acid presents the appearance of the colour unless a larger excess of hydrochloric acid is added.

Ammonium molybdate in nitric acid gives a similar colouration, but the two are readily distinguished by means of the spectroscope. The titanium solutions show no blue or green in strong solutions, only orange and red remaining, whilst with ammonium molybdate the shade of the green and some of the blue are visible.

Preparation of Pure Titanic Acid.

The best plan for preparing pure titanic acid is Wöhler's; it is as follows:—Fuse the rutile or titaniferous iron with an excess of potassium carbonate at a high temperature, in a fire-clay crucible. Pour the fused mass out into a piece of sheet-iron, so as to form, on cooling, a thin cake; next, grind this to powder, thoroughly exhaust with water, which leaves the greater part of the iron undissolved, and saturate the filtrate with hydrofluoric acid. A formation of potassium fluotitanate

soon occurs in white scaly crystals resembling boracic acid. These may be rendered quite free from iron and silicium by a few crystallisations from hot water, and ammonia will then precipitate pure titanic acid from their hot aqueous solution.

Another method for the preparation of pure titanic acid is to fuse the rutile or titaniferous iron with potassium carbonate, and exhaust the fused mass with water in the manner above described. After filtering from the insoluble portion, the liquid is slightly supersaturated with hydrochloric acid added in the cold; it is then filtered if necessary. Acetic acid and dilute sulphuric acid are now added, and a brisk current of steam is passed in for several hours, the liquid being kept boiling all the time. Pure titanic acid will be precipitated.

ZIRCONIUM.

Preparation of Pure Zirconia.

The zircon or jargon is first broken up in a diamond mortar, and next reduced to an impalpable powder in an agate mortar. It is then mixed with potassium fluoride acid, and the mixture fused. In this manner a perfect resolution of the mineral is easily obtained. The potassium fluozirconate is then dissolved out from the insoluble fluosilicate by means of hot water acidulated with hydrofluoric acid. From this solution zirconia may be precipitated by ammonia.

In Messrs. Tessié du Motay and Co.'s patent for improvements in preparing zirconia for purposes of oxyhydrogen illumination, the following process is given. The zirconia is extracted from its native ores by transforming, by the action of chlorine, in the presence of charcoal, the zirconium silicate into the zirconium and silicium chlorides. The silicium chloride, which is more volatile than the zirconium chloride, is separated from the latter by the action of heat; the zirconium chloride remaining is afterwards converted to the state of oxide by any of the methods now used in chemistry. The zirconia thus obtained is first calcined, then moistened, and submitted in moulds to the action of a press with or without the intervention of agglutinant substances, such as borax, boracic acid, or clay. The sticks, cylinders, discs, or other forms thus agglomerated, are brought to a high temperature, and thus receive a kind of tempering or preparing, the effect of which is to increase their density and molecular compactness.

Of all the known earthy oxides zirconia is the only one which remains entirely unaltered when submitted to the action of a blowpipe fed by oxygen and hydrogen. Zirconia is also, of all these earthy oxides, that which, when introduced into an oxyhydrogen flame, develops the most intense and the most fixed light.

It has long been suspected that zirconia really consists of a

mixture of two or more closely allied oxides. In 1845 Svanberg announced that the zirconia contained in the various zircons from Siberia, Norway, and Ceylon, as also in the hyacinths from Espailly and Ceylon, was a compound of two or more earths, one of which he termed noria, and in a subsequent paper the same author also found this to be the case with the earth in the Greenland eudialite. His arguments—for he did not succeed in separating the earths—were founded upon his observations that the salts of zirconium did not always contain the same constant proportion of acid to base; that the oxalates, chlorides, and sulphates differed in their behaviour and solubility in certain reagents, and that the specific gravities of the natural silicates (zircon) from various localities differed greatly from one another. These observations of Svanberg, notwithstanding the promise contained in his short paper on the subject to bring forward fuller evidence, were never followed up by him, and the subsequent researches of other chemists appear to throw doubt as to their correctness in several points, as well as to render the existence of noria extremely dubious. The researches of Berlin (*Journ. f. Prakt. Chemie*, lviii. p. 145, 1858) showed that the results of the fractional precipitation of zirconium chloride by oxalic acid did not warrant the conclusions of Svanberg, and that the zirconia prepared from zircons from Frederiksvaern, Espailly, Ural, India, and from the Ceylon hyacinths and Norwegian katapleeite, behaved in similar manner with oxalic acid, and that their oxalates were easily and completely soluble in excess of that acid, and that the specific gravity and amount of zirconia obtained from the oxalates from Frederiksvaern zircon and katapleeite which he examined were identical, so that it would seem necessary to seek for some other means of separating the earths than by the employment of oxalic acid.

In 1864, Nylander, in a paper, 'Bidrag til Kännedomen om Zirkonjord' (*Acta Universitatis Lundensis*, 1864), examined the zirconia from the Norwegian eucolite, and considered that it contained two earths, which differed in their behaviour and the solubility of their double potassium sulphate salts, but he also appears to have come to no definite results as to the existence or isolation of the earths themselves.

In 1869, Mr. David Forbes, F.R.S., was induced, on the representation of Mr. Sorby that certain specimens of the oriental jargon probably contained a considerable amount of an earthy oxide different from zirconia, to examine chemically one of the jargons forwarded to him by Mr. Sorby. As the means employed appear to throw some light on the characters of the earth hitherto regarded as zirconia, the following extracts are given from Mr. Forbes's paper which appeared in the *Chemical News* for June 11, 1869 (vol. xix. p. 277):

'The fragments, which were extremely hard, were broken up in a diamond mortar, previous to being reduced to as impalpably fine a powder as possible in an agate mortar; 16.22 grains of this powder

were then thoroughly mixed with 81 grains pure anhydrous sodium carbonate, placed in a platinum crucible, and fused at the highest heat of a large air and gas blowpipe jet, after having been previously kept for two hours over a powerful Bunsen's flame, so as to "frit" it, or insure combination previous to fusion. After complete fusion, a small lump of pure sodium hydrate (about 15 grains) was, as recommended by Berzelius, carefully deposited in the centre of the fused mass, and a second similar piece added after the first had been absorbed; the fused substance became much more liquid after this addition; the heat was kept up for another half hour longer, and the whole was allowed to cool. By the above means the mineral was perfectly decomposed, and the silica so altogether transferred to the sodium that it could be completely removed by cold water, leaving no trace behind with the earths. Previous experience with the zircons from various localities, and hyacinths from Ceylon, had proved that the perfect decomposition of these minerals is often attended with considerable difficulty. The fused mass when cold was treated repeatedly with cold water in a silver vessel, decanting off the supernatant solution each time, until the silica was entirely removed, and a white powder, probably a compound of the earth with soda, remained behind. The solution, which contained all the silica, was acidified with hydrochloric acid, evaporated to dryness, and the silica determined as usual. The silica obtained weighed 5.45 grains, consequently was equivalent to 83.61 per cent. in the mineral.

'The white insoluble residue previously mentioned was found to be perfectly soluble in hydrochloric acid; in order to test if it contained any silica, the solution was evaporated to dryness and redissolved in water acidulated by hydrochloric acid, but left no trace of insoluble matter behind. From the colour of the solution being distinctly yellow, it evidently contained iron oxide, which I had scarcely expected, since the original mineral was nearly, if not altogether, devoid of colour; the solution, consequently, was a chloride of the earths of the jargon, accompanied by some iron sesquichloride.

'Berzelius many years ago devised a means of separating iron oxide from zirconia, founded upon the behaviour of their respective chlorides, the iron sesquichloride being soluble in strong hydrochloric acid, whilst that of zirconia is nearly insoluble; I had tried this process previously with zirconia from Ceylon hyacinths, and had not been satisfied with it, as the iron solution carried along with it a not inconsiderable portion of the earth. It now struck me, however, that possibly the earth so dissolved might differ in character from that contained in the insoluble chloride, and I therefore determined to make the experiment.

'The hydrochloric acid solution was consequently again evaporated until it solidified as a yellow saline mass, whereupon it was treated repeatedly with strong hydrochloric acid of density 1.188, allowing it

to stand some time, and decanting the solution as long as the fresh acid acquired the faintest yellow tinge. A yellow solution was obtained, leaving behind a snow-white chloride, crystalline in appearance, and completely soluble in water, forming a perfectly colourless solution. From this solution ammonia precipitated a flocky, but apparently rather dense, white precipitate, which, after being thoroughly washed, dried, and ignited, was of a pure white colour, and possessed a peculiar waxy look and dense appearance; it weighed 7.48 grains, and consequently amounted to 46.12 per cent. of the jargon examined. This earth appeared to be pure zirconia.

'The yellow hydrochloric acid solution was now examined, and found to contain, besides iron sesquioxide, a considerable amount of an earthy base, like zirconia. I decided to separate the iron by the tartaric acid and ammonium sulphide process recommended by Berzelius, and, consequently, the solution was first supersaturated by ammonia, which threw down a faint yellowish-white, somewhat flocculent precipitate. Tartaric acid, in excess, was then added, which dissolved at once the greater part of the precipitate, but, notwithstanding that a very large excess was added, a portion of the precipitate refused obstinately to redissolve, even upon application of heat. In order to examine this, the solution was filtered: a white, flocculent, and somewhat glutinous substance was left upon the filter, which, when well washed with hot water, dried, and ignited, weighed 1.24 grain, equivalent to 7.64 per cent. of the original mineral.

'This body, after ignition, appeared very different from the previously-obtained zirconia; it was a white powder, but did not aggregate together or form lumps having a waxy lustre on the surfaces of fracture; on the contrary, it was more pulverulent, had a dead white, or mealy, appearance, and did not appear to be of any great density.

'Ammonia was now added in excess to the tartaric acid solution, which remained clear. Upon the further addition of ammonium sulphide, the solution assumed a dark-brown colouration; but no precipitate separated before the lapse of some days, when a black deposit of iron sulphide formed, which was collected upon a filter after the greater part of the supernatant liquid had been carefully syphoned off. This iron sulphide was converted into sesquioxide, and afforded 0.04 grain, equivalent to 0.24 per cent. in the mineral. After separation of the iron, the solution was evaporated to dryness in a platinum capsule, and ignited for some time, to drive off all ammoniacal salts, and oxidise the carbon resulting from the decomposition of the tartaric acid. There then remained behind an earthy body, of a white colour, having a slight tinge of grey, which weighed 2.08 grains, or 12.52 per cent. In appearance, this earth was quite different from the zirconia, and more resembled the second earth obtained. Possibly this substance may contain a third earth analogous to zirconia, such as Svanberg

(*Ofversigt. Kongl. Vet. Acad.* pp. 34, 37, 1845) suggested was present in eudialite and certain zircons.

'The result of this examination of the jargon, when summed up, indicates its composition to be as follows :—

	In 16·22 grains	In percentage
Silica	5·45	33·61
Zirconia α	7·48	46·12
" β	1·24	7·64
" γ	2·03	12·52
Iron sesquioxide	0·04	0·24
	<hr/> 16·24	<hr/> 100·13

'The formula ZrO_2SiO_2 ascribed to zircon requires—

Silicic acid	33·77
Zirconia	66·23
	<hr/> 100·00

with which the numbers found for jargon are closely approximative.'

The results of this chemical examination must be considered as strengthening the evidence, physical and chemical, that the earth usually denominated zirconia is, in reality, a compound of two, if not more, closely allied oxides.

Separation of Zirconium from Titanium.

This separation is one of the most difficult problems in analytical chemistry. Titanic acid and zirconia, which separately may be estimated with the greatest accuracy, when together present such properties that it might be said one of these two bodies had partly destroyed the individuality of the other, since the reactions they possess when separate they no longer possess together, whilst in some cases they act quite differently. Thus, it is well known that titanic acid in the state of sulphate is completely precipitated by boiling in a diluted solution; but that when in presence of zirconia there may be, according to the proportions of the two bodies, either incomplete precipitation or none at all. Moreover, the precipitated titanic acid always retains zirconia, although the greater part remains in solution with the rest of the titanium.

Messrs. G. Streit and B. Franz say that when titanic acid is precipitated from a solution containing zirconia, by boiling with dilute sulphuric and acetic acids, the precipitated titanic acid is free from zirconia. The boiling should be performed by the aid of steam, and be continued for eight or ten hours. They experimented with a solution containing 4·23 grammes of titanic acid, and added thereto the sulphuric acid solution of 0·613 gramme of zirconia. To the solution was then added its own bulk of acetic acid, and the liquid boiled; all the titanic acid was thereby precipitated, while zirconia remained in

solution. From the filtrate the latter substance was precipitated by ammonia, and, after having been collected upon a filter, washed, dried, ignited, and weighed. The quantity obtained was very near the amount required by theory.

F. Pisani adds metallic zinc to a mixed solution of titanic acid and zirconia in sulphuric or hydrochloric acid, until the titanium is reduced to the state of titanium sesquioxide, giving the liquid a more or less intense violet colour. Titanic acid and zirconia are, under ordinary circumstances, precipitated equally by potassium sulphate; but if the titanium is previously reduced in this manner only the zirconia is precipitated. Add excess of potassium sulphate to the violet liquid, which should be small in quantity and not too acid, the zinc being still slowly attacked; leave the whole to stand for some time, then filter quickly and wash the precipitate with a solution of potassium sulphate; afterwards extract the zirconia by the usual processes. Upon dissolving this zirconia in hydrochloric acid, and adding zinc, it will be found that only a trace of titanium remains. Unfortunately, this process is not quite accurate, and cannot be used for quantitative separation.

Titanic acid may be estimated in the presence of zirconia volumetrically. The above-described violet solution of titanium is a powerful reducing agent. On pouring potassium permanganate into this liquid, titanic acid is formed, and the solution gradually loses its colour, until it becomes of a rose tint. According to the quantity of potassium permanganate it is found necessary to add, may be calculated the quantity of titanic acid, taking for each equivalent of iron to which the permanganate corresponds one equivalent of titanic acid. The following is the mode of operating as described by Pisani, to whom this process is due:—

Titanic acid in solution in hydrochloric acid is best, because, if in the state of sulphate, it is liable to be partially precipitated by the rising of the temperature before its complete reduction has been effected. The reduction should be effected in a flask, to which has been adapted a cork with a tube drawn out to a point, so as to keep the liquid from contact with the air. The quantity of liquid should not be great, and should be acidified until the disengagement of hydrogen becomes regular; then heat gently to accelerate the reduction, and when the colour of the liquid ceases to increase in intensity, leave it to get quite cold, and dilute the liquid with cold water which has been previously boiled to free it from air, as it would otherwise oxidise the titanium. As soon as the liquid is diluted, decant it into a glass without taking the zinc with it, wash the flask once or twice, and then rapidly pour in the potassium permanganate. The combined weight of titanic acid and zirconia being previously known, and the titanium being estimated volumetrically, the difference gives the quantity of zirconia. The permanganate should be previously standardised by means of iron by Margueritte's process.

If potassium fluotitanate or titanic acid in hydrochloric acid to which an alkaline fluoride has been added, is reduced by zinc, the liquid is no longer violet, but greenish, probably because a titanium sesquifluoride is then formed instead of a sesquichloride. The results of the estimation by permanganate are, however, the same in each case.

Zirconia may be detected in titanic acid by taking advantage of its reaction on turmeric paper. A solution of zirconia in hydrochloric acid colours turmeric paper orange, especially after it has been left to dry, but titanic acid, under the same circumstances, colours it brown, which prevents zirconia from being recognised. The difficulty may be overcome by reducing the titanium by zinc, as in the state of sesquioxide titanium does not colour turmeric paper, leaving the colour of the zirconia to appear alone. The paper must not, however, be left too long to dry in the air, or the titanium, passing into the state of titanic acid, would in its turn colour the paper brown.

CHAPTER IV.

CHROMIUM, URANIUM, VANADIUM, TUNGSTEN, MOLYBDENUM.

CHROMIUM.**Estimation of Chromium.**

PROFESSOR STORER has shown that chromic oxide is quickly changed to chromic acid when boiled with a mixture of concentrated nitric acid and potassium chlorate. All the chromium in $\frac{1}{2}$ gramme of chromium oxide, or of any of the ordinary chromium salts, can in this way be converted into chromic acid in a few moments; and even compounds as refractory as chrome-iron ore, or chromium oxide, which has been strongly ignited, can be oxidised in less time than would be required to complete their oxidation by the process of fusion ordinarily employed.

Mr. E. J. Stoddart, working under the direction of Prof. E. T. Thorpe, finds this method unsatisfactory for chrome-iron ores, a part of the mineral remaining unoxidised even after boiling for an hour.

Mr. A. H. Pearson, experimenting on this process, finds that the chromic acid thus formed in the wet way can be readily and accurately estimated in the form of barium chromate, if care be taken to wash the precipitated chromate with ammonium acetate, or some other saline solution in which barium chromate is insoluble. Anhydrous chromic oxide is placed in an evaporating dish, together with a quantity of nitric acid and some potassium chlorate, and covered with an inverted funnel with a bent stem. The acid is heated, and fragments of potassium chlorate are added to it from time to time, until the chromic oxide has completely disappeared. This result is attained in the course of half an hour. The acid solution is diluted with water, then neutralised with ammonia, and the ammoniacal solution in its turn treated with enough acetic acid to make it slightly acid. After the acidulated solution has become cold, a solution of barium chloride is added to it in slight excess, and the mixture is left at rest for ten or twelve hours. The precipitated barium chromate is washed by decantation with a cold solution of ammonium acetate, then collected on a filter, rinsed with water, dried, heated in a crucible to expel the last traces of water and of the ammonium-salt, and weighed.

The precipitate of barium chromate must be allowed to stand for some time before filtering, lest it pass through the pores of the filter,

and render the filtrate cloudy. The ammonium acetate employed for washing serves to dissolve any barium nitrate or barium chloride which may have been precipitated with the chromate; it has the further advantage of dissolving less of the barium chromate than pure water would.

Experiments on various compounds of chromium show that this process is tolerably exact. Estimations of chromium in different specimens of sesquioxide gave 68·81, 68·65, 68·60, 68·81 per cent. Theory requires 68·62 per cent.

Chromic acid may also be estimated by adding mercurous nitrate to its quite cold solution, neutralised with sodium carbonate or with nitric acid; the orange-red precipitate of mercury chromate should be allowed to stand for some hours before filtering, and after being washed with a weak solution of mercurous nitrate, and dried, is heated to redness in a platinum crucible, when it leaves pure green chromium sesquioxide.

Rose strongly recommends the method of Berzelius, which consists in precipitating the chromic acid by mercurous nitrate, and washing with a dilute solution of the same salt. The precipitated chromate is voluminous, and has a brown-red colour when the precipitation takes place in the cold. A better result is obtained by precipitating at a boiling heat, when the mercurous chromate almost immediately becomes highly crystalline, its colour changing to a bright scarlet. It may then be washed with the greatest ease, and ignited in the usual manner. It is absolutely necessary, in applying this method, that the mercurous nitrate used should be perfectly free from nitrous acid. Hot solutions must not be employed, on account of the reduction of chromic acid by mercurous nitrate. This reduction is not due to the temperature, but to the presence of a small quantity of nitrous acid in the mercurous nitrate employed. It is easy to avoid this source of error by dissolving the mercury in nitric acid in an open vessel, and crystallising the nitrate two or three times, using for solution dilute nitric acid which has been perfectly freed from nitrous acid by a current of air or carbonic acid. We arrive more quickly at our object when we precipitate at once at the boiling-point, and then wash with a hot dilute solution of the nitrate.

In several works on analytical chemistry it is recommended to precipitate chromic acid from its solutions by lead acetate, and to weigh the resulting lead chromate. It is, however, next to impossible to prevent the precipitated lead chromate from passing more or less through the filter so as to render the filtrate turbid.

Very accurate results may be obtained by precipitation with barium acetate at a boiling heat, adding a small quantity of strong alcohol to the liquid, washing with water containing alcohol, and igniting. The wash-water need not contain more than $\frac{1}{2}$ of its volume of alcohol. The precipitated chromate must, before filtering, be allowed to settle

completely, leaving the supernatant liquid perfectly clear. The filtrate never becomes turbid, even after all the soluble salts are washed out. Finally, it is not necessary to weigh the barium chromate upon a weighed filter. A very small quantity of the chromic acid is always reduced by the carbon of the filter in igniting, but the loss of weight is inappreciable. This method is much shorter than that which is usually employed, as the filtration and washing may be executed almost immediately after precipitation.

For the quantitative separation of uranium and chromium, in a first series of experiments, weighed quantities of potassium bichromate were mixed with much larger, but undetermined, quantities of uranium nitrate. The chromic acid was then precipitated by mercurous nitrate from the boiling solutions.

The mean of the analyses was 51.73 per cent., which is precisely the percentage required by the formula.

Detection of Chromates and Free Chromic Acid.

To detect a monochromate along with a bichromate add to a few c.c. of the boiling solution a drop of a moderately concentrated solution of manganese sulphate. In presence of monochromate a blackish-brown precipitate is formed. Bichromate in monochromate is detected by adding to a boiling solution of sodium thiosulphate an equal volume of a hot solution of the chromate in question. A brown precipitate or a distinct turbidity proves the presence of bichromate. The precipitate is chromic oxide. Free chromic acid in a solution of bichromate is detected by adding a solution of potassium iodide and shaking with carbon disulphide, which is coloured a deep purple by the liberated iodine.

Estimation of Chromium as Phosphate.

Chromium may be exactly determined as phosphate, and this method is often convenient. On boiling a solution of a chromium salt slightly acidified, to which has been added an alkaline phosphate and sodium acetate, the whole of the chromium is precipitated as phosphate. This method succeeds both with the green and the violet salts, chlorides and sulphates, and with the acetates, but not with the oxalates. It is also suitable for alkaline chromates, but in this case the action of the phosphoric acid must be combined with that of sodium thiosulphate, which acts as a reducing agent. The solution of chromate, to which is added a sufficient quantity of phosphoric acid, or of a phosphate, then of acetate, and lastly of thiosulphate, and which has been slightly acidified, is boiled for about an hour: it deposits all the chromium as phosphate, with a little sulphur derived from the thiosulphate. The phosphate precipitated is a green hydrate. It may be washed with boiling water, or preferably with hot solutions, first, of

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ammonium acetate, followed by ammonium nitrate. On calcination it turns grey, and contains chromic oxide in the proportion of 51.86 per cent.

Volumetric Estimation of Chromium in the Presence of Ferric Oxide and Alumina.

If a solution of permanganate is made strongly alkaline with sodium carbonate and a little caustic soda, heated to a boil, and a neutral solution of chromic oxide is run in, the chromic oxide is at once converted into chromic acid, whilst manganese peroxide is separated out. The process is completed when the supernatant fluid has the pure yellow tint of alkaline chromates without the slightest reddish tinge, which may be recognised with sufficient distinctness.

The presence even of considerable quantities of ferric oxide and alumina in the solution containing chromium does not prevent the completion of the reaction from being distinguished, since these oxides, if precipitated in a hot solution, are rapidly deposited along with the manganese peroxide. If the approximate relation of the alkaline permanganate to the chromium solution in question has been determined by a preliminary experiment, on further titration the end of the reaction can be observed with sufficient accuracy. In fact the volumetric determination of chromium is in this manner rendered possible without the previous separation of iron and alumina.

Volumetric Estimation of Chromic Acid.

Add to the chromic acid solution a sufficient quantity of potassium iodide, free from iodate, and pure hydrochloric acid. This mixture is left quietly standing for from half an hour to a few hours' time, according to the degree of concentration of the solution, for in no case is the reduction of the chromic acid by means of the hydriodic acid instantaneous. When the reduction is complete, which may be learned from the pure green colour the liquid has assumed, a small quantity of thin starch paste is added, and the quantity of iodine which has been set at liberty is estimated by titration with a solution of sodium thiosulphate. This plan, first proposed by C. Zulkowsky, gives sufficiently accurate results, and in some cases may be found useful; but it requires care, and is inferior to gravimetric estimation.

Another method has been devised by Mr. W. J. Sell, and yields rapid and accurate results. The solution, containing chromium acidified with sulphuric acid, is boiled and a dilute solution of permanganate added to the boiling liquid until a purplish tint remains after boiling for three minutes. The solution is then rendered slightly alkaline with sodium carbonate, alcohol is added, and the manganese filtered off. The chromic acid in the filtrate is estimated by titration with iodine and sodium thiosulphate.

For the valuation of chrome iron ores, see Iron.

Separation of Chromium from Aluminium.

A. Carnot has shown that aluminium can be exactly separated from chromium by converting the latter into an alkaline chromate, acidifying the solution slightly with acetic acid, and adding an excess of sodium phosphate. The mixture is boiled and filtered to separate the aluminium phosphate. When this is done, it is easy to determine the chromium by pouring into the liquid, thiosulphate, and, if needful, a further quantity of alkaline phosphate, and boiling. The precipitate of chromium phosphate is then washed, ignited, and weighed.

URANIUM.

Estimation of Uranium.

H. Rose¹ recommends the employment of ammonium sulphide as a precipitant for uranium, as it completely separates this metal from its solutions, provided they are previously saturated with ammonia. No inconvenience attends the presence of a quantity of ammoniacal salts in the solution, excepting, of course, ammonium carbonate and alkaline carbonates in general. The precipitate is black, but with a large excess of sulphide it may be reddish-brown. It is to be washed with water containing a little ammonium sulphide. The precipitate contains no uranium sulphide, but consists essentially of uranium protoxide.

After desiccation it is roasted, to expel any sulphur which may adhere to it; it is then calcined at a high temperature in a current of hydrogen, and left to cool.

Pure uranium protoxide is thus obtained. Should the solution contain much potassium salts, or other strong non-volatile base, the precipitate may retain a little of them.

If a rapid process is required for the estimation of the commercial value of uranium, the following process of Patera's will give sufficiently accurate results, although it is not so trustworthy as the one just described.

A weighed quantity of the mineral is dissolved in nitric acid, taking care not to employ a large excess of acid. The solution is diluted with water, and, without filtering, supersaturated with sodium carbonate. It is now boiled to complete the solution of the uranium, and to promote the separation of the iron, lime, &c. carbonates. The filtered solution of uranium oxide in sodium carbonate now contains only traces of foreign substances, and the uranium will be precipitated in the form of sodium uranate with an excess of acid, on the addition of caustic soda. The orange-yellow precipitate is collected on a filter, washed for a short time, and then dried. It is then removed from the filter and heated to redness in a platinum crucible, the ashes of the filter, burnt apart, being added to the precipitate. The mixed residues

¹ *Pogg. Ann.* cxvi. 352.

are now placed on another filter and again washed, dried, and ignited, as before. The residuum of this second calcination is acid sodium uranate, from the weight of which the amount of uranoso-uranic oxide in the mineral may be calculated. 100 parts of the sodium uranate represent 83 parts of uranoso-uranic oxide.

Volumetric Estimation of Uranium.

The author prefers Guyard's process for this estimation, which depends on the precipitation of an insoluble triple ammonium, uranium, and manganese phosphate, when an acid solution of manganese phosphate is added to an acid solution of uranium and ammonium acetate.

The test solution of manganese phosphate is prepared as follows:—Phosphoric acid solution of a syrupy consistency is heated in a platinum dish, and manganese sesquioxide in fine powder is added by degrees, stirring frequently. The mixture is then heated for some time, and when the fused mass assumes a blue tint, and the phosphoric acid begins to volatilise, it is allowed to cool. It then becomes purple, and if dissolved in water it forms a purple solution resembling that of a permanganate. This solution is diluted, so that 80 c.c. shall represent 1 gramme of metal. The tinctorial power of manganese phosphate is very weak.

To titrate this solution use a known quantity of pure uranium sesquioxide in the form of acetate. The precipitate appears white with a yellowish shade. As soon as the precipitation is complete the precipitate has a rose colour. It must be remembered that the presence of ammonium oxalate interferes with the reaction.

To apply this process to ores, &c., dissolve a gramme or more of the substance in nitric or hydrochloric acid, or a mixture of the two. The solution is then supersaturated with ammonium carbonate, which separates uranium sesquioxide from the metallic oxides which so often accompany it. In many cases this operation suffices; but if the ore contains phosphorus or arsenic, or an oxide soluble in ammonium carbonate, the uranium must be precipitated by ammonia and ammonium sulphide in the state of protoxide, as already described, and filtered off. The precipitate is dissolved in ammonium carbonate, and then transformed into the acetate of the sesquioxide. In any case the uranium must be brought into this state before estimation; but oxalic acid must be absent.

The solution is now diluted with about a litre of cold water, and then the standard solution of manganese phosphate is gradually added from a burette until the whitish precipitate of uranium, manganese, and ammonium phosphates appears rose-coloured. This process is very rapid, and with a little practice is accurate.

In testing for uranium with potassium ferrocyanide, it must be borne in mind that the presence of ammonium oxalate prevents the formation of the red precipitate.

Separation of Uranium from the Cerium Metals.

Wolcott Gibbs's method of precipitating the cerium metals with sodium sulphate in the form of double sodium sulphates with cerium, lanthanum, and didymium will effect this separation perfectly. These double sulphates are insoluble in a saturated solution of sodium sulphate, whilst the double sulphate sodium and uranium sesquioxide is readily soluble, and may be easily washed out from the highly crystalline insoluble double sulphates of the cerium group.

Separation of Uranium from Chromium.

The author's analyses show that mercurous nitrate gives very accurate results. The employment of this salt in separating chromium from uranium is indicated only in those cases in which the chromium exists as chromic acid, in which relatively small quantities of chlorine or sulphuric acid are present, and in which no other acid is present which, like phosphoric acid, gives an insoluble mercurous salt not completely volatilised by ignition. In the presence of chlorine, sulphuric acid, &c., the following process may be very advantageously employed. The solution is to be boiled for a few minutes with a small excess of sodium hydrate, the precipitate of sodium uranate filtered off and washed with hot water containing a little sodium hydrate, until the washings no longer give any turbidity with a solution of mercurous nitrate. The sodium uranate in the filter is then to be dissolved in hydrochloric acid and the uranium determined in the usual manner. The filtrate contains all the chromium. After adding hydrochloric acid in excess, the chromic acid may be most conveniently reduced to chromic oxide by adding a solution of potassium or sodium nitrite and boiling for a few minutes, after which the oxide may be precipitated by ammonia in the usual manner. An alkaline nitrite is a better reducing agent than alcohol, as the chromic oxide may be precipitated immediately after the reduction.

It remains to consider the case in which chromic and uranic oxides occur together in solution. A solution of sodium hydrate in small excess is to be added, and the whole heated to boiling. To the hot liquid bromine-water is to be added. Chromium oxide is almost instantly oxidised to chromic acid, which remains in solution, while sodium uranate, with a small percentage of uranic chromate, remains undissolved. After washing with hot water containing a little sodium hydrate, the precipitate, which has a deep orange colour, is to be dissolved in hot nitric acid, the solution boiled for a few minutes to expel any traces of nitrous acid, mercurous nitrate added, and the whole allowed to stand until the small quantity of mercurous chromate has settled. This, after washing, may be ignited in the same crucible with the chromic oxide obtained as above from the sodium chromate in the filtrate. The filtrate is free from uranium.

Separation of Uranium from most Heavy Metals.

Uranium may be easily separated by H. Rose's method from metals which are precipitated from their solutions by ammonium sulphide, in the following manner :—Add to the solution an excess of ammonium carbonate mixed with sulphide. All the oxides which the sulphide transforms into sulphides are precipitated, while the uranium protoxide is dissolved in the ammonium carbonate. Leave it to deposit in a closed vessel, wash the precipitate by decantation in water containing ammonium carbonate and sulphide, and filter. Gently heat the filtered liquid to expel most of the carbonate, decompose the sulphide by hydrochloric acid, oxidise the uranium protoxide with nitric acid, and precipitate the uranium oxide by ammonia. If the operation is quantitative it should, before weighing, be calcined in a current of hydrogen.

Separation of Uranium from Phosphoric Acid.

In laboratories where the estimation of phosphoric acid by the uranium process is frequently practised, it occasionally becomes advisable to effect the separation of uranium from the acid. M. Reichardt describes the following plan, which has proved very successful in the author's laboratory :—Dissolve the uranium phosphate in hydrochloric or nitric acid, apply heat, add excess of iron perchloride, and next, excess of solution of sodium carbonate, wherein, aided especially by the large quantity of carbonic acid which is thus set free, the uranium oxide is readily dissolved, while the phosphoric acid is combined in an insoluble form with the iron oxide. The solution of uranium oxide in sodium carbonate is acidified with hydrochloric acid, boiled to expel carbonic acid, and the uranium oxide finally precipitated with ammonia.

He has since proposed the following modification :—He dissolves the uranium phosphate in sodium carbonate, and precipitates with a magnesium salt. If the precipitate of uranium phosphate is old, it is necessary to dissolve it first in hot concentrated hydrochloric acid, adding nitric acid to peroxidise any iron present. The solution is then heated and soda added in excess. After a new filtration the phosphoric acid is thrown down by adding ammonia and magnesium chloride. After twenty-four hours the liquid is separated from the ammonio-magnesium phosphate. It is acidified with hydrochloric acid, heated, and the uranium oxide precipitated by ammonia, avoiding excess.

VANADIUM.

Detection of Vanadium.

Mr. Richard Apjohn uses the following process :—8 grammes of the finely-powdered mineral is fluxed with four times its weight of sodium carbonate. The fused mass is allowed to cool, and a small

quantity of nitre added. It is now heated over a Bunsen lamp, taking care that the crucible does not attain more than a dull red heat. The mass is lixiviated with water, and the aqueous solution boiled with ammonium carbonate and filtered to remove silicic acid. The filtrate is evaporated with hydrochloric acid, and sulphuretted hydrogen passed in to precipitate any metals of the lead group which might be present. The filtered solution is then heated with an equal volume of very concentrated solution of ammonia, and sulphuretted hydrogen is passed in till all the free ammonia is saturated.

The solution assumes a beautiful intense cherry-red colour, a sure indication of vanadium. This coloured liquid is filtered off and saturated with hydrochloric acid; the precipitate, containing sulphur and vanadium sulphide, is dried and ignited, and the residue melted with nitre. From the potassium vanadate thus formed the characteristic blowpipe reactions are obtained.

For the analysis of vanadium sulphates Dr. B. W. Gerland proceeds as follows:—To estimate the sulphuric acid, vanadium and alkalis, the weighed sample is dissolved in water, according to circumstances, with the aid of nitric acid or ammonia, or both. After cooling, the clear solution is acidulated with nitric acid, mixed with lead acetate and alcohol until all sulphuric acid is precipitated. After a few hours' rest, when the lead sulphate has settled, it is filtered and washed with dilute alcohol. No difficulty is experienced if the vanadium is present as tetroxide, but with the pentoxide it often happens that lead vanadate is mixed with the sulphate, and is recognisable by the intense yellow colour of the latter. In that case only the clear liquor is poured off and passed through a small filter, the precipitate treated with a little nitric acid, if necessary heated in a water-bath, then mixed with water and afterwards with alcohol, and allowed to stand for a few hours. The vanadate is generally dissolved by this treatment, and the lead sulphate appears perfectly white; it is now thrown on the same filter and treated as before. But it does happen, particularly when the precipitation has taken place at a higher temperature, that the sulphate still retains a small amount of vanadate. Ammonium carbonate is the most efficient means for separating this small residuum. The solution of this reagent scarcely acts upon the pure lead vanadate; but if the latter is mixed with lead sulphate the former is left intact, whilst the sulphate is rapidly converted into lead carbonate. The solution, therefore, contains all the sulphuric acid, and only inappreciable traces of vanadium; it is treated with barium chloride in the usual way, and the barium sulphate weighed. The insoluble part, after washing, is heated with acetic acid to dissolve the lead carbonate, and the remaining vanadate is thrown upon the filter already used, washed, and united to the main vanadium precipitate.

The solution from the lead sulphate is neutralised with ammonia, acidulated with acetic acid, and precipitated with lead acetate in small

excess. If vanadium tetroxide is present, as shown by the dark colour of the precipitate, it is necessary to oxidise it, and this is readily effected by the addition of bromine water. The precipitate will now be of a bright orange or yellow colour, and very bulky; but heating, assisted by agitation, causes it to contract to a heavy curdy mass. In this condition it can be easily filtered and washed on a Bunsen filter under a low pressure. It is of advantage to add a small amount of lead acetate to the wash-water. The precipitate is dissolved in nitric acid, the solution treated with sulphuric acid and alcohol, and after a few hours' rest separated from the lead sulphate, which after washing is free from vanadium, as Roscoe has already pointed out. The filtrate containing the vanadium is evaporated in a porcelain basin, at a very low temperature (the water-bath at boiling-heat would cause a very lively evolution of gas, and loss, particularly when sulphuric acid is added in great excess), the residuum transferred to a platinum dish, again evaporated, and the sulphuric acid driven off by carefully raising the temperature. All the vanadium sulphates (those of the trioxide, tetroxide, and pentoxide) leave vanad-pentoxide at red heat. But this is readily reduced at that temperature by dust, and even by the gases from the lamp; it is therefore necessary to cover the capsule well, and prevent the access of fire gases, which is best accomplished by the use of a Rose's tube. The heat is then increased to a bright red, which again causes an evolution of gas, and leaves a pure pentoxide, whose weight is taken. (If the vanadium sulphates are decomposed at a dark-red heat, until gas-bubbles cease to appear, the pentoxide gives off gas again, when the heat is raised and loses weight amounting to about 0.5 per cent.) The platinum vessel suffers in shape by this operation. A dish which was used very often had originally a flat bottom, but now the latter is pressed out by the vanadium pentoxide, so that the form is hemispherical, and at least 3 millimetres deeper.

The filtrate from the lead vanadate contains, besides the alkalies, a small amount of vanadium. Vanadium solutions behave, as I have ascertained, similarly to those of cobalt under the influence of sulphuretted hydrogen, a dilute acetic solution with small excess of free acid, particularly in presence of an alkaline acetate, is slowly acted upon by that gas, and the vanadium precipitated as vanadyl sulphide. If the filtrate, therefore, is treated with sulphuretted hydrogen, according to Roscoe's direction, the vanadium which it contains will be separated with the lead sulphide; it is on that account preferable to use sulphuric acid and alcohol for the elimination of the lead. The filtrate from this lead sulphate is evaporated, and the residuum heated until the ammonium salts are driven off. The remaining alkalies are dissolved, treated with acetic acid, and once more submitted to the described process for the separation of the small quantity of vanadium with lead acetate. The filtrate from this lead vanadate precipitate is most ex-

peditionously treated with ammonia and ammonium sulphide at boiling-heat, and the solution separated from the lead sulphide is worked up for the estimation of the alkalis.

The Estimation of Vanadium by Titration with Permanganate.

The first condition is the conversion of vanadium to a certain stage of oxidation. Aqueous sulphurous acid converts vanadium pentoxide in solution to tetroxide, which is perfectly unchangeable in acid liquors, so that these can be boiled for the expulsion of the excess of sulphur dioxide. The tetroxide solutions undergo a further reduction, which, if not guarded against, might make the test fallacious. I shall shortly be able to refer more fully to this process, but I mention here briefly that the tetroxide in solution, containing an excess of sulphuric acid, is converted into vanadium trioxide by carbonaceous matter (which is introduced by alcohol or with dust), and by sulphur at a temperature of 120° , and that at higher temperatures (about 150°) the acid vanadium sulphate separates in the form of insoluble needles, and at about 200° the yellow vanadium sulphate appears as a heavy amorphous sediment mixed with the former. If such conditions are apprehended it is necessary to add permanganate until the test-solution remains pink after boiling, as proof that all vanadium is oxidised to the pentoxide, then to treat with sulphurous acid, and, after expelling the excess, titrate again with permanganate.

The colouration obtained by the permanganate generally disappears after a short time, and is reproduced by the first drop of this solution, to bleach again, and so on, until, after a large quantity (up to 20 per cent. of what was used to produce the first pink) has been added, the solution becomes opaque by the separation of manganic peroxide. In every case the first appearance of the pink colour is the indication that all vanadium is converted into the pentoxide, and the quantity of permanganate used corresponds exactly with that required by an equivalent quantity of oxalic acid. In hot solutions the first appearance of pink is permanent. The reaction of the permanganate solution takes place instantaneously the colour changes from blue, through green, to yellow and pink, indicating at every stage the quantity of the standard solution required. The titration of vanadium with a standard solution of permanganate is in fact one of the most elegant, expeditious, and accurate methods of volumetric analysis.

Detection of Vanadium in Iron Ores.

R. Boettger heats the finely-powdered ore to redness for a long time with nitre and sodium carbonate. He lixiviates with boiling water and almost neutralises with nitric acid, free from the lower oxides of nitrogen, leaving the solution slightly alkaline. The bulk of

the alumina and silica falls down. The filtrate is treated with barium nitrate, when barium vanadate is thrown down, from which vanadic acid is easily separated.

Preparation of Vanadic Acid from Lead Vanadate.

For the following method the author is indebted to the late Professor Wöhler:—Finely pulverise the mineral and attack it with a mixture of concentrated hydrochloric acid and alcohol; wash the precipitated lead chloride with alcohol, and drive off the hydrochloric acid by means of heat from the blue solution of vanadium chloride. This solution, treated by excess of caustic soda, deposits vanadium oxide, which may be converted into vanadic acid by a current of chlorine.

For the following method of preparing vanadic acid on the large scale from the cobalt bed sandstone at Mottram, the author is indebted to Sir Henry Dr. Roscoe, whose researches on the chemistry of this metal (*Phil. Trans.* 1868, p. 1, and 1869, p. 679) have afforded so great an insight into the properties of this remarkable element.

The sandstone possesses a light colour, and contains from 0.1 to 0.3 per cent. of the cobalt, nickel, and copper oxides. These metals are extracted commercially by the Alderley Edge Copper Mining Company; the ore is crushed and digested with hydrochloric acid; bleaching liquor and milk of lime are then added to alkaline reaction; a portion of the copper, together with the whole of the nickel and cobalt, remains in solution, whilst the small portion of vanadium which the ore contains falls down in the precipitate. It was from this precipitate that Sir H. Roscoe was fortunate enough to secure a plentiful supply of this rare metal. A rough analysis of the crude lime precipitate showed that it contained about 2 per cent. of vanadium, together with lead, arsenic, iron, lime, and sulphuric and phosphoric acids.

In order to prepare pure vanadium compounds in quantity from this material, 3 cwts. were dried and then finely ground with four times its weight of coal, and the mixture well furnaced with closed doors for several days until the greater part of the arsenic had been driven off. The coal having been thus burnt off, the mass was then ground up with one quarter of its weight of soda-ash, and well roasted in a reverberatory furnace with open doors for two days to oxidise the vanadium to a soluble vanadate; the mass was then lixiviated, and the solution drawn off from insoluble matters; the liquid was acidified with hydrochloric acid, and sulphurous acid was then passed into the solution to reduce the arseniates, when the remaining arsenic was precipitated by sulphuretted hydrogen. The deep-blue solution thus obtained was carefully neutralised by ammonia (an excess causes much of the vanadium to pass into solution), the precipitated vanadium oxide washed on cloth filters, oxidised by nitric acid, and evaporated to dryness. The well-dried crude vanadic acid was then boiled out with a saturated solution of ammonium carbonate, which left iron oxide, calcium

sulphate, and aluminium sulphate insoluble, and the filtrate evaporated until the insoluble ammonium vanadate separated out. This crude vanadate was then washed with sal-ammoniac solution to free it from sodium salts, and recrystallised.

In order to prepare pure vanadic acid from this salt, it was roasted in the air, and the powdery acid obtained was suspended in water into which ammonia gas was passed; the dissolved ammonium vanadate was separated by filtration from a residue containing silica, phosphates, &c., and was crystallised by evaporation in platinum.

Another method of preparing pure vanadic acid is to obtain the pure oxychloride, and decompose this by water, when vanadic acid is yielded as a fine orange-coloured powder. The oxychloride is prepared by intimately mixing sugar charcoal with crude vanadic acid, and heating the mixture to redness in a current of hydrogen. After cooling in hydrogen, the mixture of trioxide and carbon is removed to a hard glass retort heated by a large Bunsen's lamp, and a current of dry chlorine gas passed in. The crude oxychloride comes off as a reddish-yellow liquid, which is purified by distillation in a current of carbonic acid, and afterwards rectified several times over clean sodium. It is a yellow-lemon liquid, boiling at 126.7°C .

Purification of Vanadic Acid from Phosphorus.

Sir H. Roscoe has found that phosphorus is very difficult to separate from vanadium. The action of even traces of phosphoric acid on vanadic acid is most remarkable; if present in quantities exceeding 1 per cent. of the weight of the vanadium, it altogether prevents the crystallisation of the vanadic acid, and the fused mass possesses a glassy fracture and a black vitreous lustre. If much phosphorus is contained with the vanadium, the method which has proved most effectual for its removal is to deflagrate the finely-divided impure acid with its own weight of sodium in a well-covered wrought-iron crucible, and wash the resulting mixture of vanadium oxides by decantation until the wash-water ceases to give an alkaline reaction; frequently this operation has to be repeated three times before the molybdenum test ceases to indicate phosphorus.

Detection and Estimation of Vanadium and Titanium in Basalts.

Mr. G. Roussel proposes the following process:—The samples, in fine powder, are fused with thrice their weight of sodium carbonate; the mass, when cold, is powdered, and treated with water acidulated with hydrochloric acid; it is evaporated to dryness, heated for twenty-four hours on the water-bath, treated again with acidulated water, and then filtered. The silica eliminated is, after calcination, set to digest for twelve to eighteen hours in hot concentrated sulphuric acid, treated after cooling with an excess of cold water, and filtered. This

operation is repeated, and the total liquid is mixed with ammonia, which throws down titanous acid. It is filtered, washed, and ignited. The liquid separated from the silica also contains titanous acid. To separate it, it is treated with sodium sulphate, sulphurous acid, and sodium thiosulphate, boiled for twenty minutes, and there is left the mixed precipitate of sulphur, alumina, and titanous acid. The sulphur is driven off by gentle heating, and the residue is mixed with the former precipitate, and digested in a sealed tube with pure hot concentrated hydrochloric acid, in order to eliminate the alumina. After this series of operations, the titanous acid is pure, and may be dried and weighed. The same basalts contain vanadium, but in a far smaller proportion. To obtain a ponderable quantity, it is necessary to operate upon a sample twenty times larger than is required for the detection of titanium. The basalt is melted with sodium carbonate and the mass oxidised with a little saltpetre. After cooling, the pulverised mass is treated with a large quantity of boiling water, filtered, and washed perfectly. The liquid is evaporated, boiled with ammonium carbonate and filtered, treated with ammonium sulphide, and left to settle for two or three days. If the solution contains vanadium, at this moment the fine red colour of vanadium sulphide, when dissolved in an alkaline sulphide, appears in the liquid. It is filtered, and hydrochloric acid is poured into the liquid, which throws down vanadium sulphide mixed with sulphur. The latter disappears on careful heating, when the vanadium sulphide, VS_2 , is weighed. The largest percentage of titanium was 2.878, and that of vanadium 0.028.

TUNGSTEN.

Preparation of Tungstic Acid from Wolfram.

The following process, due to Professor Wöhler, has been found to answer very well. Reduce the wolfram (an iron and manganese tungstate) to fine powder, and digest at a gentle heat in a mixture of four parts strong hydrochloric and one part nitric acid, till yellow pulverulent tungstic acid is left behind. Wash this by decantation, dissolve in ammonia, and evaporate the solution to the crystallising-point. The resulting ammonium tungstate calcined in the air leaves pure yellow tungstic acid.

When the impure tungstic acid is dissolved in ammonia, a residue will be left which contains, besides undecomposed wolfram, small white grains composed of silica and niobic acid, and constituting about 2 per cent. of the wolfram.

MOLYBDENUM.

Detection of Molybdic Acid.

M. O. Maschke has improved the process of Schoenn. According to the latter, traces of molybdic acid and its compounds may be dis-

covered by the blue colouration produced on heating it with concentrated sulphuric acid in a porcelain capsule. This test is rendered exceedingly convenient and much more certain by the following modification:—A little concentrated sulphuric acid is applied to a piece of platinum foil, bent so as to form a slight depression; upon the acid is placed a little of the substance in powder, and the foil is heated till vapours escape in abundance; it is then allowed to cool, and repeatedly moistened with the breath. When, after cooling, only minute spots are visible, the sulphuric acid, after being breathed upon, takes an intense blue colouration. On heating the platinum foil, the blue colour vanishes, but reappears on cooling. It is completely decolourised if a considerable quantity of water is added.

Estimation of Molybdic Acid.

T. M. Chatard proceeds as follows:—Add to the boiling solution of the molybdate, lead acetate in slight excess. Boil for a few minutes; the precipitate, at first milky, will become granular and will subside easily, leaving a perfectly clear supernatant liquid. Care must be taken in boiling, as the thick milky fluid is very apt to boil over. A ribbed filter is to be used, and the precipitate is to be washed with hot water. The washing proceeds with great ease and thoroughness, and not the slightest milkiness should be apparent in the filtrate. The precipitate is dried at 100°, separated from the filter and ignited in a porcelain crucible.

The process gives very good quantitative results and is both easy and expeditious. The precipitated molybdate separates easily from the filter, and can be heated to low redness without decomposition.

Separation of Molybdic Acid from Phosphoric Acid.

E. Reichardt dissolves the phospho-molybdic compound in sodium carbonate, and precipitates by means of magnesia mixture; the solution is treated with *aqua regia*, and evaporated to dryness to expel excess of acid. The residue is then treated with water, which leaves the molybdic acid undissolved.

CHAPTER V.

ZINC, ALUMINIUM, IRON.

ZINC.

Precipitation of Metallic Zinc.

WHEN metallic magnesium, as met with in commerce, is introduced into a slightly acidulated solution of zinc sulphate (or other zinc salt) hydrogen is evolved, and a precipitation of a spongy bulky mass of metallic zinc occurs. If this sponge is washed till free from soluble salts, then dried and pressed in a steel crushing-mortar between the jaws of a powerful vice, a brilliant solid lump of zinc is produced.

Volumetric Estimation of Zinc.

When a solution of a zinc salt is added to a known quantity of solution of potassium ferrocyanide, there is formed a precipitate of zinc ferrocyanide, insoluble in ammonia. By estimating the amount of potassium ferrocyanide remaining in solution by means of potassium permanganate, the amount of zinc present can be readily calculated. Upon this reaction M. Renard has based the following process:— Dissolve a known weight (1 or 2 grammes) of the substance to be assayed for zinc in aqua regia, add excess of ammonia, filter from the precipitate and wash well. To the filtrate 25 c.c. of a solution of potassium ferrocyanide (150 grammes to the litre) are added; the solution is made up to 250 c.c., and filtered; 100 c.c. of the filtrate are measured into a glass vessel, and neutralised with pure hydrochloric acid free from chlorine and sulphurous acid. Afterwards the solution is rendered strongly acid with about 30 c.c. of the same acid and titrated permanganate solution added until the whole of the yellow prussiate is transformed into red prussiate. By calculation the amount of zinc contained in the substance is arrived at. None of the metals commonly present in minerals, such as iron, aluminium, manganese, lead, &c., influence the process. Either they are precipitated by the ammonia, or they are not precipitated by potassium ferrocyanide. Copper is an exception, and, if present, interferes with the process.

A good method for volumetrically estimating the amount of zinc in ores is given in the *Zeitschrift für Analytische Chemie* for 1869,

by Maurizio Galetti, Chief Assayer at the Royal Assay Office, Genoa. The following is a description of the process :—Supposing zinc sulphide (blende) is to be assayed, about half a gramme of the finely-pulverised ore is to be treated with concentrated nitric acid, and boiled to incipient dryness, until the sulphur left undissolved does not contain any particles of undissolved ore. Then add strong hydrochloric acid, and boil again until no nitric acid is left. Calamine (zinc carbonate) should at once be acted upon with hydrochloric acid; but, in order to make sure of the complete oxidation of all the iron the ore may happen to contain, it is best to add to the acid a few decigrammes of pure potassium chlorate. After having boiled this solution for a few minutes, it is diluted with distilled water; a large excess of ammonia is added to the solution, which is then boiled and slightly acidified with acetic acid. After brisk agitation, boil again for a few minutes, and then supersaturate with ammonia. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to half a litre. This having been done, the fluid is very cautiously and gradually acidified with dilute acetic acid, one part acid sp. gr. 1·07, to 10 of distilled water. Any large excess of this should be avoided, as the solution should only be very slightly acid. As soon as the basic iron acetate has subsided, the precipitation of the zinc by means of a standard solution of potassium ferrocyanide may be proceeded with.

The ferrocyanide solution is made by dissolving 41·25 grammes of the said salt in as much distilled water as will make the solution weigh exactly one kilogramme.

The presence of lead compounds (as, for instance, lead carbonate, sulphate, or sulphide) occurring along with the ores of zinc, does not interfere with the completeness of the precipitation of zinc as zinc ferrocyanide. This even holds good up to 10 per cent. of metallic lead. Since some zinc ores, especially calamine, often contain manganese, it is best to add to the ammoniacal solution, before any acetic acid is added, a few drops (from 2 to 4) of bromine, in order to convert the manganese protoxide into proto-sesquioxide, leaving the solution standing for twenty-four hours after the addition of the bromine.

The ammoniacal solution of zinc chloride being colourless, there should be added to it, previous to cautious acidification by means of dilute acetic acid, a few drops of tincture of litmus, in order to more readily hit the precise point of sufficient acidification, which is known by the blue colouration changing to a rose-red.

The zinc ferrocyanide which is mixed with iron oxide preserves its naturally white colour as long as the liquid contains free zinc, but its colour changes to a greyish-white as soon as a very slight excess of the standard ferrocyanide solution is present; the liquid also then becomes turbid, and the precipitate settles very slowly. By these characteristic signs the end of the operation may be always recognised.

In order to make sure, the liquid should be touched with a glass rod which has been just previously moistened with a dilute solution of ammoniacal copper nitrate; this will have the effect of indicating any excess of the ferrocyanide solution, by producing the more or less intense colour characteristic of copper ferrocyanide. The zinc solution should be at a temperature of from 40° to 50° , whereby the rapid subsidence of the zinc ferrocyanide is promoted.

Filtration is not necessary, as the presence of the gelatinous silica (due to the decomposition of zinc silicates occurring in the ores of that metal) does not interfere with the correctness of this method of estimating zinc quantitatively.

C. Mann converts the zinc into chloride and mixes with a few drops of a concentrated solution of iron-ammonium alum, and with an excess of standard silver nitrate. By titrating back with ammonium sulphocyanide till a faint redness is remarked, the excess of silver is ascertained, and consequently the quantity of silver used to precipitate the chlorine, and by reducing the latter to zinc the amount of this metal is known. The zinc is converted into chloride as follows:—It is dissolved in nitric acid, mixed with ammonium acetate, sulphuretted hydrogen gas is passed through the solution, and the precipitate, after boiling and twice decanting, is filtered. The precipitate, along with the filter, is placed in a beaker, mixed with about 50 c.c. of water and an excess of well-washed silver chloride, and boiled till the liquid becomes perfectly clear. The precipitate, a mixture of silver sulphide and excess of silver chloride, is easily washed. When this is complete the filtrate is acidulated with nitric acid and treated as above.

Mr. F. Maxwell Lyte considers that an advantage will be found by the employment of a uranium salt as an indicator in the estimation of zinc volumetrically, by means of ferrocyanide. The zinc should be in solution, in hydrochloric acid by preference, and the solution should be pretty strongly acid. Iron or copper should not be present, nor should nickel or cobalt.

When a solution of zinc in hydrochloric acid is heated to 80° or 100° C., rendered pretty strongly acid, and a drop or two of uranium acetate added, and then a solution of potassium ferrocyanide run in from a burette, a brown spot of uranic ferrocyanide forms where the potassium ferrocyanide falls, but disappears on stirring, so long as a trace of zinc remains unprecipitated; but the moment all the zinc has become converted into ferrocyanide, the next drop or so of potassium ferrocyanide tinges the whole liquid brown. Mr. Lyte prefers, in practice, not only adding a trace of uranium acetate to the zinc solution, but at the same time—at the end of the operation—trying a drop of the zinc solution on a white porcelain plate, with a glass rod moistened with the uranium salt. The reaction seems in this case slightly more delicate, while the operator is warned of the approach of the termina-

tion by the fact that the brown colour in the liquid disappears rather more slowly towards the end of the operation.

Mr. C. Fahlberg also proposes to titrate zinc in a hydrochloric solution with potassium ferrocyanide, and uses as indicator a solution of uranium nitrate, which, as soon as an excess of ferrocyanide appears in the solution, gives a brown precipitate, or at least a brown colouration. Manganese and alumina do not interfere. After dissolving the ore in aqua regia, all metals precipitable by sulphuretted hydrogen, and also iron, are removed by the ordinary methods. The ammoniacal solution containing the zinc is neutralised with hydrochloric acid, and then acidulated with 10 to 15 c.c. of the same acid at sp. gr. 1.12. This solution is titrated with a solution of ferrocyanide, of which 1 c.c. represents 0.01 gramme of zinc; the final reaction is performed on a porcelain plate upon which a series of drops of a solution of uranium nitrate have been placed. The results are exact to 0.2 or 0.3 per cent.

In the sodium sulphide process M. O. Schott recommends glazed card-paper (containing lead carbonate) as an indicator.

Estimation of Zinc as Oxalate.

A very ingenious method of estimating zinc as well as other metals, and one which, in the author's hands, has proved very accurate, has been worked out by Mr. W. Gould Leison, of the Lawrence Scientific School. The process is as follows:—The zinc compound is obtained in the form of a sulphate, and to a neutral solution of this salt oxalic acid and then a large quantity of strong alcohol are added. Zinc oxalate precipitates in the form of an extremely fine powder. This is filtered through sand, thus: A slight funnel is ground conical near the throat. A little pear-shaped piece of glass with a long stem is then dropped into the funnel, stem upwards, so as to form a valve, impassable to sand laid upon the ball of the glass, but allowing liquids to pass freely. By means of the stem the valve can be lifted from its seat, and the sand and zinc oxalate, after washing with alcohol and careful drying, are washed together into a flask with hot dilute sulphuric acid. A few c.c. of strong sulphuric acid are then added, and the solution titrated with potassium permanganate. From the amount of oxalic acid thus found the quantity of zinc can readily be calculated.

Estimation of Zinc as Sulphide.

All who have experienced the difficulty of filtering and thoroughly washing the light, slimy precipitate of zinc sulphide, as ordinarily obtained, will be glad to know of a modification of the usual mode of precipitation (due to Mr. J. H. Talbot, of the Lawrence Scientific School), whereby this difficulty is avoided. The solution of zinc, if acid, is to be neutralised as nearly as possible by sodium or ammonium

carbonate. To the boiling solution sodium or ammonium sulphide is to be added, a large excess being very carefully avoided. The white precipitate, on continued boiling, soon becomes granular, and settles readily. The supernatant clear liquid is then to be tested with a drop of the alkaline sulphide, to be sure of complete precipitation, and the sulphide then washed with hot water. The filtrate is perfectly clear and quite free from zinc; the washing is easy and rapid. The zinc sulphide is next to be partially dried with the filter, brought into a porcelain crucible, and ignited, at first gently and afterwards strongly, with free access of air. The expulsion of the last traces of sulphuric acid is much facilitated by occasionally dropping fragments of ammonium carbonate into the crucible. Pure zinc oxide finally remains, the ignition being continued until a constant weight is obtained. The results in this way are very accurate.

A New Method of Estimating Zinc.

According to Hugo Tamm, when a solution of zinc in any mineral or volatile organic acid is supersaturated by ammonia, until all the zinc oxide is dissolved, and when this solution is re-saturated by hydrochloric acid until litmus paper indicates a feeble acid reaction, a double zinc and ammonium chloride exists in the liquor. If a solution of ordinary crystallised sodium phosphate is added, a voluminous white precipitate of zinc phosphate is formed, which, if left for a few minutes at a temperature near the boiling-point of the liquor, soon combines with ammonium phosphate, and suddenly comes down as a dense white precipitate, which settles very rapidly.

This precipitate of ammonio-zinc phosphate, collected on a filter, can be washed with the utmost facility, in fact, as fast as water can be poured upon it, and it never passes through filters, a most important property. It retains the sodium phosphate and ammonium chloride in the midst of which it has been precipitated with some strength, and several successive washings are absolutely required to free it from these salts, but eventually the washing is complete. To ascertain this, silver nitrate acidulated with nitric acid must be used, because the double phosphate retains chlorides with more strength than phosphates. After drying at 100°C. , the ammonio-zinc phosphate contains exactly 86.49 per cent. of metallic zinc.

Calcined over a gas-lamp, the double phosphate leaves a residue of zinc pyrophosphate.

It might be supposed that zinc could be estimated with accuracy in this salt; but this is not the case, as a loss of zinc is always incurred during the calcination of the ammonio-zinc phosphate. On the contrary, the composition of the zinc and ammonium phosphate, well washed and dried at 100°C. , can always be relied upon, and it is from the weight of this salt that the amount of zinc must be calculated.

The precipitation of zinc is complete when the supernatant liquid,

mixed with a little excess of sodium phosphate, does not show any bulky precipitate of zinc phosphate; but it is advisable to add at once to the zinc solution a quantity of sodium phosphate sufficient to turn red litmus paper blue. The liquor is only momentarily alkaline, and it reassumes its slightly acid or neutral reaction as soon as the double phosphate has come down, so that the precipitation actually takes place in a slightly acid or neutral liquor—a gratifying result.

Should a very accurate estimation of zinc be required, the liquor should be left in a warm place for some ten or twelve hours, when the precipitation of the zinc will be very complete, as might be proved by adding ammonium sulphide to the filtrated liquor, or sulphuretted hydrogen to the filtrate previously saturated by ammonia, and reacidulated by acetic acid. In general a trace of zinc is precipitated, for the double phosphate is not absolutely insoluble. For most practical purposes, it is quite sufficient to allow the precipitated double phosphate to rest for about an hour; a very small quantity of zinc will remain in the liquor, from which it can be separated by ammonium sulphide, but this quantity of zinc never amounts to more than $\frac{1}{360}$ of the quantity of zinc precipitated by sodium phosphate, so that it can be neglected, especially if a simple assay of zinc is all that is required.

One of the chief defects of the double phosphate is its propensity of adhering firmly to the side of the flask in which the precipitation takes place. A thin film of this salt coats the glass, and it can be removed only with some difficulty. A glass stirrer, covered at one end with 1 inch or $1\frac{1}{2}$ inch of indiarubber tubing, can be advantageously employed for this purpose. But it is best, after the bulk of the precipitate has been removed on the filter, to dissolve the adhering film in dilute hydrochloric acid, to neutralise by ammonia, to add a few drops of sodium phosphate, to boil, and to add the slight precipitate thus obtained to the main portion already placed on the double filter.

It is sometimes possible to avoid the coating of the glass with ammonio-zinc phosphate, by heating the solution almost to boiling-point before adding sodium phosphate: the precipitation in this case is very rapid, and, by taking this precaution, further trouble is avoided. But the chief defect of this mode of estimating zinc is undoubtedly the use of sodium phosphate, a fixed salt, difficult of separation from most substances. Unfortunately, with zinc, there is no choice of precipitating reagents, and sodium phosphate, which must be considered as a very perfect assay reagent, is, from its very nature, a defective one in analytical researches.

Estimating the Value of Zinc Powder.

V. Drewsen prepares two solutions; the one of pure fused potassium bichromate—say 40 grammes per 1000 c.c.—and the other of crystalline ferrous sulphate, about 200 grammes in 1000 c.c. The iron solution must be strongly acidulated with sulphuric acid, to prevent

oxidation. In order to find the respective value of the two liquids, 10 c.c. of the iron solution are measured into a beaker, a little sulphuric acid is added, and the other solution is dropped in from a burette until a drop of the mixture is no longer turned blue by potassium ferricyanide. About 1 gramme of the zinc powder is then weighed, placed in a beaker with 100 c.c. of the chromic solution, 10 c.c. of dilute sulphuric acid are added, the whole is well stirred, 10 c.c. more of the sulphuric acid are added, and allowed to act for about a quarter of an hour with diligent stirring. When everything is dissolved except a small insoluble residue, an excess of sulphuric acid is added, and 50 c.c. of the iron solution in order to reduce the greater part of the excess of chromate; more of the iron solution is then added from a burette till a drop displays a distinct blue reaction with ferricyanide, and the mixture is then titrated back with chromate till this reaction disappears. From the total number of c.c. of the iron solution consumed the quantity is deducted which corresponds to the ferrous solution employed. The chromate contained in the remainder, if multiplied by 0.6611, shows the metallic zinc contained in the powder.

To determine the metallic zinc present—the only valuable constituent—Fresenius mixes about 8 grammes of the powder in a flask with sulphuric acid, and passes the hydrogen gas evolved through refrigerating and desiccating tubes into a combustion-tube filled with cupric oxide. The water formed is absorbed in a U-tube two-thirds full of broken glass and containing 12 c.c. pure concentrated sulphuric acid. Nine parts of water correspond to 32.58 parts of metallic zinc.

J. Barnes estimates the value of the zinc powder by the amount of hydrogen evolved. The hydrogen is measured by the quantity of water which it displaces. The gauge consists essentially of a narrow graduated tube placed in mercury; on the upper end of the tube a bulb is blown. The value of the graduations is determined. On exposing this bulb to the temperature and pressure at which the gas is being measured, reading off the division at which the mercury inside and outside is level, and referring to a table, a number is obtained. The observed volume of the gas is divided by this number, and the corrected volume at once obtained.

Separation of Zinc from Uranium.

To a nearly neutral and somewhat dilute solution of the two metals add sodium acetate in excess, boil, and pass sulphuretted hydrogen through the boiling solution till all the zinc is precipitated as sulphide. Filter quickly, wash, and finish as described at page 120.

Separation of Zinc from Chromium.

Obtain the zinc and chromium sesquioxide in the form of a nearly neutral solution, by the addition, if necessary, of sodium carbonate, then add excess of sodium acetate, and oxidise the chromium to the

state of chromic acid by a current of chlorine, or (if it be present in small quantity only) by addition of chlorine water, or bromine. The solution should be kept hot and as neutral as possible by the cautious addition of sodium carbonate. When the oxidation is complete expel the excess of chlorine or bromine by heat, and add barium acetate, which will precipitate the whole of the chromium present in the form of barium chromate, taking the precautions already described at page 101.

The oxidation of the chromium to the state of chromic acid may also be effected by Professor Storer's method, with nitric acid and potassium chlorate, as described at page 101.

Separate the excess of barium from the solution by addition of sulphuric acid, and then precipitate the zinc with sodium carbonate; or the acid solution may be supersaturated with ammonia so as to redissolve the zinc oxide, filtered, if necessary, to remove iron, &c., and the zinc precipitated by sulphuretted hydrogen. When barium sulphate and chromate are thrown down together, the chromic acid may be reduced to sesquioxide by boiling with concentrated hydrochloric acid and alcohol, after which the barium may be precipitated by sulphuric acid, and the chromium sesquioxide thrown down in the filtrate by boiling with ammonia in the usual manner. As the reduction of barium chromate by means of hydrochloric acid and alcohol does not take place very readily, it is better to boil the chromate with an excess of potassium or sodium carbonate, to filter off the barium carbonate, and determine the chromic acid by means of mercurous nitrate, as explained at page 108, or by reduction to chromium oxide and precipitation with ammonia in the usual manner.

ALUMINIUM.

Detection of Alumina.

Mr. Beckmann recommends baryta-water in preference to the caustic alkalies, as not being contaminated with alumina and silica. Solution of ammonium chloride is afterwards added as usual.

Precipitation of Alumina.

Ammonium sulphide is a more complete precipitant for alumina than caustic ammonia or ammonium carbonate, and should always be employed in preference when practicable. The small quantity of free sulphur which will be generally precipitated at the same time is driven off on ignition. It must be remembered that oxalic acid and its salts possess in a slight degree the property of most non-volatile organic acids, of impeding certain reactions of alumina; therefore, when ammonium oxalate is present in great excess, alumina is not immediately precipitated by ammonia and ammonium sulphide; although, in the course of a little time, according to its proportion, alumina is precipitated, especially if the solution be heated.

Assay of Clays for Alum Making.

Mr. G. Pouchet proceeds as follows:—A mean sample of 50 grammes is taken and placed in a tared platinum or porcelain capsule. It is submitted to a moderate calcination. When it has attained a dull redness, the capsule is withdrawn, let cool, and weighed. The loss indicates the proportion of moisture and of volatile matters (combined water and organic matter). Upon the calcined clay are then poured 100 grammes of sulphuric acid at 60° B., the whole is well mixed with a glass rod, and heated till it becomes solid. It is then lixiviated with boiling water, and the alumina is determined in the ordinary manner in a known part of the solution.

Separation of Aluminium from Zinc.

The metals should preferably be in the form of chlorides. Dilute the solution considerably, render it neutral or nearly so, add sodium acetate in excess, and then boil for a short time, adding a drop of free acetic acid occasionally; the whole of the aluminium will be precipitated in the form of basic acetate. Filter rapidly through a ribbed filter, and keep the liquid as near the boiling-point as possible during filtration. If an absolutely complete separation is necessary, redissolve the precipitate in dilute hydrochloric acid and repeat the operation. From the solution the zinc is completely precipitated by sulphuretted hydrogen.

Separation of Aluminium from Uranium.

The separation of these two metals may be effected in the same manner as that of aluminium and zinc above described.

Separation of Aluminium from Chromium.

To a strong solution containing these two metals add potassium chlorate and concentrated nitric acid; the chromium is quickly oxidised to chromic acid. Or the same thing may be effected by means of chlorine or bromine, as described at page 128. The chromic acid is then precipitated with barium chloride, taking the precautions described at page 101. With care, this process gives very accurate results.

Another, and under some circumstances, a better plan, is the following, for which the author is indebted to Professor Wöhler. Pass chlorine through the solution of the chromium and aluminium sesquioxides in caustic potash, until all the chromium is oxidised to chromate. The aluminium will then be in the form of precipitated hydrate, with the exception of a small quantity, which is readily precipitated by digestion with ammonium carbonate. Filter the solution of potassium chromate from the alumina, and to the filtrate add alcohol and excess of hydrochloric acid, and heat till the reduction to chromium sesqui-

oxide is complete. Add ammonia to the warm solution, when the whole of the chromium will be precipitated as sesquioxide.

A. Carnot proposes, in order to separate alumina as phosphate from chromium sesquioxide, to transform the latter first into chromic acid by fusion with pure potash and nitre. It is then dissolved, and the liquid is acidified slightly with nitric acid. A little sodium phosphate and sodium acetate are then added, and the liquid raised to a boil. The aluminium phosphate is precipitated alone. It is washed with boiling water in order to remove all the chromic acid, redissolved in nitric acid, and the determination of the alumina is completed as above. The filtrate is raised to a boil, and there is gradually poured into it aluminium nitrate enough to throw down all the phosphoric acid. It is boiled for half an hour and filtered. The filtrate when cold is mixed with lead acetate, when the chromic acid is precipitated and weighed as lead chromate.

Separation of Aluminium from Glucinum.

These metals may be separated by precipitating the aluminium in the form of basic acetate, as described at page 124 (Separation of Aluminium from Zinc). The glucina may be precipitated in the filtrate by ammonia.

Dr. Wolcott Gibbs adds a solution of sodium fluoride to the one of aluminium and glucinum, when the whole of the aluminium is thrown down in the form of cryolite, while the glucinum remains in solution. From this solution ammonia precipitates the glucina.

When sodium thiosulphate is added to a nearly neutral dilute solution containing aluminium and glucinum, and the liquid is boiled until no more sulphurous acid is disengaged, alumina is precipitated (together with some sulphur), whilst the glucinum remains in the solution.

Separation of Aluminium from the Cerium Metals.

Bring the metals to the form of sulphates dissolved in a small quantity of water, and add sufficient powdered sodium sulphate to form a saturated solution. The cerium metals immediately separate in the form of double sulphates with sodium sulphate, as a white highly crystalline powder. Filter off and wash with a saturated solution of sodium sulphate. Precipitate the aluminium from the filtrate by addition of ammonia and ammonium sulphide, and dissolve the double sodium and cerium sulphates, &c., in dilute hydrochloric acid, and precipitate with ammonium oxalate.

Separation of Aluminium from Magnesium.

These, when in solution together, may be separated by Dr. Gibbs's plan, viz. boiling the dilute solutions with excess of sodium acetate and a little acetic acid, whereby all the aluminium is precipitated as

basic acetate. The details of the operation are conducted as in the Separation of Aluminium from Zinc (page 124).

Insoluble mixtures containing aluminium and magnesium, such as spinel (magnesium aluminate), are best analysed by the process given by Wöhler. Fuse the finely-levigated mineral with six times its weight of potassium bisulphate, and keep the mass fused at a red heat till sulphuric acid is no longer disengaged. Dissolve the fused mass in water acidified with hydrochloric acid, and decompose it with sal-ammoniac, which precipitates the alumina. To prevent any magnesia coming down with the alumina, care must be taken to keep the liquid boiling till no more free ammonia is given off. The gelatinous alumina, which the boiling liquid deposits, is filtered, but as it is almost impossible to wash in this state, it must be allowed to half dry on the filter, when it can be washed perfectly. The magnesium is precipitated from the filtrate by ammonia and sodium phosphate.

Separation of Aluminium from Calcium.

The method of separating calcium from aluminium by means of ammonia has been improved by H. Rose. Instead of being careful to employ ammonia free from carbonic acid, and avoiding the presence of this gas, he heats to gentle ebullition the liquid in which the alumina has been precipitated by excess of ammonia. When the evolution of ammonia ceases, all the aluminium is in the precipitate, and may be separated by filtration without requiring any special precaution, for the simple reason that in the presence of ammoniacal salts the calcium carbonate is decomposed, the calcium entering into solution. A little sal-ammoniac may even be added, if there is a chance of there not being sufficient to favour this decomposition.

When the calcium is present in small quantities only, tartaric acid may be added, and the solution then supersaturated with ammonia. The calcium is precipitated in the form of tartrate if there is only a little aluminium present; otherwise, much remains in solution. In either case, however, ammonium oxalate will separate it perfectly in the form of calcium oxalate.

GALLIUM.

Detection of Gallium.

To test for Gallium in a blende the mineral is attacked by nitro-hydrochloric acid, excess of acid expelled by boiling, and the solution treated with pure zinc in the cold. The solution is filtered while there is still a notable evolution of hydrogen, and the filtrate boiled with zinc. The precipitate that is formed is washed, dissolved in hydrochloric acid, and the solution, as concentrated as possible, is tested spectroscopically. If necessary, the operation of boiling with zinc is repeated on the first white deposit formed.

For a blende containing the average amount of gallium, 10 grammes of the mineral are sufficient to obtain distinctly the principal ray of gallium.

Compounds of gallium—the chloride in particular—give in the spectroscopie two very characteristic rays, one of which especially is sufficiently brilliant to reveal feeble traces of this element. The hydrated chloride produces in the gas flame but a very feeble and fugitive spectrum.

In order to obtain a sensitive reaction it is necessary to have recourse to the induction spark which is taken off the surface of the solution, employing a spark of 1·5 to 2 millimetres long.

The characteristic bands in wave-lengths are :—

509·	.	.	A nebulous band of moderate intensity, only seen with concentrated solutions of Ga_2Cl_3 .
417·	.	.	Sharp, intense.
403·1	.	.	Distinct, but much less intense than 417·.

Separation of Gallium from Potassium, Sodium, Lithium, Cæsium, Rubidium, and Ammonium.

When the proportion of gallium is not very small, the simplest method is to supersaturate the hydrochloric solution with ammonia, and to boil until litmus paper, previously placed in the liquid, takes a distinctly red tint. Water must be added to make up for the loss by evaporation. The gallium oxide is received upon a filter, washed, dried, and ignited. To separate the traces of gallium entangled in a considerable mass of alkaline salts, the boiling solution is treated with cupric hydrate. The mixture of gallium sesquioxide and cupric oxide is redissolved in a decided excess of hydrochloric acid; the copper sulphide, which is then thrown down by sulphuretted hydrogen, does not carry gallium with it, and the liquid concentrated to a small bulk is supersaturated with ammonia, and then boiled for a long time.

Separation of Gallium from the Alkaline Earths.

If the gallium is moderately large in quantity it may be at once precipitated by ammoniacal supersaturation, followed by prolonged boiling; the alkaline earthy oxides remain in solution. Traces of gallium sesquioxide mixed with much of the barium, strontium, or calcium salts, are separated by means of cupric hydrate. The baryta and the bulk of the strontia and lime may also be precipitated by sulphuric acid from a liquid more or less alcoholic. After evaporation of the alcohol and concentration to a small bulk, the gallium is recovered by ammoniacal ebullition, or by cupric hydrate, according to the degree of exactness required. When the former method has been used the precipitate must be ignited strongly to expel completely any traces of sulphuric acid.

Separation of Gallium from Magnesium.

Prolonged ebullition of a solution supersaturated with ammonia succeeds well. The process with cupric hydrate is suitable where there are small quantities of gallium along with much magnesium.

Separation of Gallium from Zirconium.

The boiling solution is treated with excess of solution of potash. The precipitate of zirconia requires prolonged washings, and retains traces of gallia, which are extracted by re-solution in hydrochloric acid and reprecipitation by potash. Two or three treatments with boiling potash generally suffice. The gallium oxide is freed from potassic salts by supersaturation, first with hydrochloric acid, and then with ammonia and prolonged boiling, or more accurately by means of cupric hydrate. Only feeble traces of zirconia pass into the alkaline solution, which are separated from gallium by potash at the end of the analysis.

Arsenious sulphide also effects the separation of zirconium and gallium, and is especially useful to detect small traces of gallium masked by much zirconium. The liquid charged with acid ammonium acetate and arsenious acid is treated with sulphuretted hydrogen, as already indicated.

Ferrocyanide cannot be used, as it gives a canary-yellow precipitate in solutions of zirconium, even if very acid and very dilute. Ebullition even does not effect the solution of the precipitate in a liquid containing two-thirds of its bulk of concentrated hydrochloric acid. This fact is mentioned because some chemical treatises assert that potassium ferrocyanide gives a precipitate in neutral solutions of zirconium, but not in such as are acid.

Separation of Gallium from Uranium (Yellow Uranic Salts).

The four following methods are suitable for exact analyses :—

1. The hydrochloric solution, slightly acid, is treated at a boil with an excess of cupric hydrate. The deposit contains all the gallium as well as a very sensible portion of uranium. It is redissolved in hydrochloric acid, diluted with water, and boiled in presence of a large excess of cupric hydrate. With from 10 to 15 parts of uranium to 1 of gallium four successive precipitations are required. The uranium is then entirely contained in the liquids, which are acidified, and are then traversed by a current of sulphuretted hydrogen. Copper sulphide is deposited, and the salt of uranium is obtained on evaporating the filtrate.

2. If there is iron to remove along with uranium it is first reduced by heat with metallic copper, and then boiled with an excess of cuprous oxide. Four successive operations suffice to separate completely 1 part gallium from 10 to 15 parts uranium. The presence of

very considerable quantities of alkaline salts does not interfere with the execution of the two methods just described, which may serve for the analysis of a mixture of gallium and of an alkaline uranate.

8. The hydrochloric solution, slightly acid, is mixed with an excess of ammonium acetate, as also a certain quantity of zinc free from gallium, and is then treated with a current of sulphuretted hydrogen. The zinc sulphide carries down the gallium, whilst the uranium remains in solution. Only the zinc sulphide, being very difficult to wash, ought to be redissolved in hydrochloric acid and reprecipitated in an acetic solution. The gallium is separated from the zinc, as described below. The uranium is separated by evaporating the liquids with an excess of hydrochloric acid to expel acetic acid, and then destroying the ammoniacal salts with aqua regia. It is essential to add to the liquid so much zinc chloride that the zinc sulphide may carry down all the gallium. Some drops of zinc chloride should be added to the filtered sulphuretted liquids to ascertain the absence of gallium in this last zinc sulphide. Alkaline salts do not interfere with the separation of uranium and gallium by means of zinc sulphide. The present process is suitable for the detection of small traces of gallium in large masses of uranic compounds, especially in presence of metals such as aluminium. But in ordinary cases it is better to make use of the reactions of copper hydrate or of metallic copper and cuprous oxide.

4. Uranium may be precipitated by a slight excess of caustic potash as an alkaline uranate, scarcely retaining a slight trace of gallium, which may be entirely removed by redissolving in hydrochloric acid and reprecipitating with potash. The alkaline liquids collected contain all the gallium and traces of uranium. These liquids are slightly supersaturated with hydrochloric acid, mixed with an excess of cupric hydrate and raised to a boil, when the gallium is completely precipitated. In the filtrate copper, uranium, and potassium are separated by known methods. When the potash employed contains a little carbonate (a frequent case) the proportion of uranium not precipitated is sensibly increased. This is without inconvenience, since the separation of this gallium and of the dissolved uranium is effected afterwards by the action of cupric hydrate.

Separation of Gallium from Zinc.

The hydrochloric solution very strongly acid is supersaturated with ammonia and boiled till it reddens litmus, the water driven off being replaced. Care must be taken that the liquid when cold does not cease to redden litmus, which will happen if traces of zinc oxide remain unattacked. If the gallium oxide retains a little zinc oxide it is redissolved by hydrochloric acid in excess, and the boiling with ammonia is repeated. Cupric hydrate separates gallium accurately from zinc. The process is conducted with the aid of heat on principles already

laid down. In case of need the operation is repeated. When in addition to zinc iron is present in the solution, it is better to reduce with metallic copper and precipitate with cuprous oxide. The separation is as exact as with cupric hydrate. The zinc being much more readily eliminated than the iron, the latter metal is the chief object of concern.

Barium and calcium carbonates precipitate gallium oxide in the cold, but the deposits contain considerable quantities of zinc oxide, especially if barium carbonate has been used. These two reagents can only be employed when it is required to concentrate gallium into a small volume, and cannot be admitted in an exact analysis. The same observation applies to the precipitation of gallium by calcium carbonate at a boil after sulphurous reduction. There is much zinc in the deposit, however short the boiling has been, especially if the excess of calcium carbonate is considerable. The treatment with calcium carbonate in heat, after reduction with sulphurous acid, though not suitable for analysis, is very advantageous for the extraction of gallium from its ores, since by repeating the process two or three times we may eliminate almost all the zinc, the greater part of the iron and many other bodies.

Separation of Gallium from Aluminium and Chromium.

The most convenient process is to precipitate the gallium with ferrocyanide from a very acid hydrochloric solution, containing at least from a fourth to a third of its bulk of concentrated acid. When the gallium is in small proportions (less than $\frac{1}{100000}$), it must be allowed to stand one day or two days for the precipitate to form. It is then received on a filter, and washed with water containing a fourth to a third of its bulk of hydrochloric acid. The filter is dried at a gentle heat and ignited. The result is a mixture of the gallium and iron oxides, which are separated, as will be explained in a subsequent chapter. The almost inevitable formation of a little Prussian blue in the highly acid liquid presents no inconvenience, and merely increases the proportion of ferric oxide to be afterwards separated from the gallium oxide. Ferrocyanide enables us to separate and determine gallium mixed with 2000 times its weight of aluminium or chromic oxide. Nevertheless, slight traces of gallium diffused among enormous masses of alumina or chromic oxide may escape the action of the ferrocyanide. They are collected then by entanglement in metallic sulphides (those of zinc, arsenic, or manganese) formed in alkaline or acetic solutions. Precipitation with sulphuretted hydrogen in a solution containing ammonium acetate, free acetic acid, and arsenious acid seems preferable. The galliferous arsenic sulphide, previously washed with sulphuretted hydrogen water containing a little acid ammonium acetate, is treated with aqua regia, and evaporated almost to dryness in presence of an excess of hydrochloric acid

to expel nitric acid. The arsenic acid is then reduced by sulphurous acid or an alkaline sulphite, diluted with water strongly charged with hydrochloric acid, and treated with sulphuretted hydrogen. The precipitated arsenious sulphide is washed with sulphuretted hydrogen water containing hydrochloric acid. The gallium remains in the liquid, and is separated by concentration to a small bulk, and boiling after supersaturation with ammonia.

Reactions of Gallium.

The following are the relative sensibilities of the principal reactions as given by Lecoq de Boisbaudran :—

1. **Metallic Zinc.**—One-sixth of a milligramme of gallium is easily separated without sensible loss from a litre of liquid, even in presence of many foreign substances. At this degree of dilution we are still far from the limit of the sensitiveness of this method. The difficulty of procuring pure zinc unfortunately restricts in practice the use of this metal in delicate analyses.

2. **Cupric Hydrate.**—The same sensitiveness as zinc.

3. **Copper and Cuprous Oxide.**—The same exactitude as the two former. Copper and its oxides, being easily obtained in a state of purity, are to be recommended whenever their use is practicable.

4. **Arsenic Sulphide.**—Very sensitive, but perhaps slightly inferior to the three former reactions. It withdraws the greater part of $\frac{1}{8}$ of a milligramme of gallium from a litre of liquid.

5. **Manganese Sulphide.**—With $\frac{1}{8}$ milligramme gallium per litre we obtain at the end of the operation the ray Gaa 417, but less bright than if we had made use of arsenic sulphide.

6. **Potassium Ferrocyanide.**— $\frac{1}{80000}$ of gallium is precipitated and collected upon a filter without sensible loss; we may therefore go further.

7. **Boiling after Supersaturation with Ammonia.**—This process gives rise to losses, which seem to range between 1 and 1.5 milligramme per litre. In a rigorous analysis the ammonia is expelled in the water-bath, or the mixture is boiled in a flask placed in a slanting position to prevent loss by spiring.

8. **Calcium Carbonate, hot, then Ammoniacal Ebullition of the Hydrochloric Solution of the Mixture of Calcium Carbonate and Gallium Sesquioxide.**—The losses, slightly higher than those in the preceding method, rise to 1.5 milligramme per litre of the liquid.

9. **Calcium Carbonate, hot, after Reduction of the Liquid with Sodium Sulphite, then Ammoniacal Ebullition of the Hydrochloric Solution of the Mixture.**—The loss is about 1.5 milligramme per litre.

IRON.

Preparation of Pure Iron.

The preparation of metallic iron in an absolutely pure state is a problem of enormous difficulty. The British Association appointed a committee, consisting of Sir F. A. Abel, Dr. Forbes, and Dr. Matthiessen, to investigate the subject. The plan finally adopted by the committee was as follows:—Pure dried iron protosulphate and pure dried sodium sulphate are mixed in nearly equal proportions, and introduced gradually into a red-hot platinum crucible. The mass is kept in fusion until the evolution of sulphurous acid gas ceases. The crucible is then allowed to cool, and the fused mass is extracted with water. If the heat be properly regulated, the whole of the iron is left as a very fine crystalline oxide. This oxide is thoroughly washed by decantation, to remove every trace of the sodium sulphate, and after being dried, is reduced by hydrogen in a platinum crucible; the spongy iron thus obtained is pressed into solid buttons by means of a strong coining-press and a diamond mortar, and then melted in lime crucibles, the lime having been previously burnt, slaked, and reburnt, thus forming a fine impalpable powder, which is compressed in the crucible mould. The best method of fusion has been found to be as follows:—The lime crucible is placed in a slanting position on a piece of lime. A large oxyhydrogen blowpipe plays on the outside of the crucible, whilst the flame of another is directed inside. When white-hot a cylinder of the compressed iron is thrown into it. It quickly melts, but at the expense of a large quantity of the iron which is oxidised, the amount so lost varying between 25 and 50 per cent. In order to obtain a good solid button of melted iron, it is necessary to cool it in an atmosphere of hydrogen, which is easily obtained simply by turning off the oxygen from the blowpipe playing inside the crucible. On analysis it was found that buttons so prepared, weighing about 15 grammes each, were free from phosphorus, silicon, and calcium, and only contained sulphur to the extent of from 0.00025 to 0.0007 per cent.

Metallic magnesium put into a solution of a proto- or sesqui-salt of iron, causes an evolution of hydrogen, and a precipitation of metallic iron in the pulverulent state. When freed from the saline solution by washing, then dried and compressed, this metallic sponge possesses great brilliancy, and dissolves in acids without leaving any residue, and without communicating any odour to the hydrogen. As the distilled magnesium of commerce is almost chemically pure, and as salts of iron can readily be freed from impurities by crystallisation or other means, this affords a good method for obtaining pure iron. The compressed metallic sponge is consolidated, as above described, by heating in lime crucibles before the oxyhydrogen blowpipe.

Estimation of Iron as Ferric Oxide.

In most laboratories the flocculent precipitate of hydrated ferric oxide is collected on paper filters—a very tiresome operation. In order to collect this precipitate Sergius Kern uses a thin platinum funnel. The tube of the funnel is closed by asbestos-wool previously ignited and weighed. The solution is next filtered and the precipitate washed. The funnel is then placed on a sand-bath, and when the precipitate is dry the bottom part of the funnel tube is closed by means of a platinum stopper, and the whole is next ignited and weighed. Knowing the weight of the asbestos and of the funnel, the weight of the ferric oxide may be calculated. In this way the weight of many flocculent precipitates in a dry state may be estimated in a quick and convenient manner.

To Dissolve Ignited Ferric Oxide.

Instead of fusing insoluble ferric oxide with sodium bisulphate, A. Classen prefers to boil it with dilute caustic potash. As soon as the previously pulverulent mass becomes flocculent, the alkaline liquid is decanted off and the oxide dissolved in concentrated hydrochloric acid.

Estimation of Iron Protoxide in the Presence of Peroxide.

Messrs. Wilbur and Whittlesey have carried out a suggestion of Avery,¹ and applied it very successfully to the estimation of ferrous and ferric oxides in silicates. Avery found that silica and many silicates can be readily and completely dissolved by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

These chemists have applied this observation to the estimation of the two iron oxides, and have obtained such satisfactory results that their process deserves to be generally adopted for the estimation of iron in silicates. The method is as follows:—A quantity of the finely-powdered silicate to be examined is weighed in a platinum crucible; as much, or rather more than as much, powdered fluor spar (or powdered cryolite), free from iron, is poured into the crucible; the powders are thoroughly mixed by stirring with a glass rod; the rod is wiped clean upon a fresh portion of the powdered fluoride; and the latter is thrown upon the mixture in the crucible. Strong hydrochloric acid is then poured into the crucible, until the powder is thoroughly drenched and the crucible about two-thirds filled with the liquid. The crucible is set upon a water-bath, and heated until the iron has all dissolved; the proportion of iron is finally determined by titrating with a standard solution of potassium permanganate. To protect the mineral from the air during the process of solution, the crucible must be kept full of

¹ *Chemical News*, vol. xix. p. 270.

some non-oxidising gas, which can be either carbonic acid or coal gas, as may happen to suit the convenience of the operator.

If carbonic acid be used, it is sufficient to cover the crucible with a bit of sheet-lead, perforated with two holes, through one of which is thrust a glass tube communicating with a gas-bottle in which the carbonic acid is generated, while the other serves as an outlet for the escape of carbonic acid and acid vapours. The crucible is, in this case, simply set upon an ordinary water-bath.

When coal-gas is used (and this agent is to be preferred on the whole), the apparatus may be arranged as follows:—Set the charged platinum crucible upon a glass or leaden tripod, inside a wide beaker, in the bottom of which there is about an inch of water. Invert a narrower beaker within the first, so that its mouth shall be sealed by the water and the crucible be enclosed in a transparent chamber. Coal-gas is led into this chamber through a bent glass tube, which passes down between the side of the upright and that of the inverted beaker, and delivers the gas near the top of the chamber. The surplus gas escapes through another tube similarly bent, which starts from a point below the crucible, and is burned in the outer air. To facilitate the passage of the glass tubes, the mouth of the inverted beaker may be made to rest upon three or four bits of stone or metal, or an orifice large enough to admit the tubes may be made upon the rim of the beaker. During the process of solution, the upright beaker is kept immersed in water, at or near the temperature of boiling. In case the coal-gas should contain any sulphuretted hydrogen, it would be well to purify it by means of a potash-tube. An hour and a half is ample for the solution of the iron in 0.5—1 gramme of finely-powdered trap rock. Fifteen minutes, on the other hand, will suffice for the solution of 0.2 gramme of iron wire. Instead of hydrochloric acid, sulphuric acid may be used to act upon the mixture of fluor spar and mineral. The calcium sulphate frequently formed is objectionable, from its liability to envelope portions of the mineral, and to protect the iron from being dissolved, rather than from any tendency to interfere with the actual titration.

Experiments have shown that the presence of iron sesquioxide does not interfere in any way with the estimation of the protoxide. Commercial iron-alum, which of itself has no decolourising action on potassium permanganate, has none after it has been heated with cryolite and hydrochloric acid. It is found, also, by acting upon weighed quantities of iron wire mixed with cryolite and iron-alum, that the iron can be estimated as well in the presence of the alum as in its absence, provided only that the metallic iron be dissolved in hydrochloric acid, with the necessary precautions to prevent oxidation, before adding the other ingredients of the mixture. If the iron wire, cryolite, and ferric alum were treated all at once with acid, some of the hydrogen generated by the solution of the metallic iron would reduce

a part of the ferric salt ; so that, in the final titration, more iron would be found than was introduced into the mixture in the form of wire.

If time enough be allowed, finely-powdered iron sesquioxide can be dissolved in this way, even after intense ignition.

To estimate iron sesquioxide in a silicate a separate portion of the mineral may be treated with fluor spar and acid, the solution reduced by zinc in a small flask in the usual way, and the total amount of iron determined with permanganate. Or, if the mineral contains only a small proportion of ferric oxide, it will be sufficient to put a bit of zinc into the crucible with the mixture of mineral, fluor spar, and acid. The difference between the total iron and that determined as protoxide is calculated as peroxide.

A. H. Allen has pointed out that a little irregularity in the results of the above process arises from the employment of hydrochloric acid as a solvent. It has been repeatedly shown that the presence of hydrochloric acid interferes appreciably with the estimation of iron by permanganate, while it does not affect Penny's bichromate process. If the former oxidising agent be employed, the solution should be effected by means of sulphuric acid.

Mr. Allen effects solution of difficultly soluble ores by heating with hydrochloric acid under pressure. This method has been used very successfully in the analysis of various titaniferous iron ores and sands. About a gramme of the finely-powdered mineral is heated in a sealed piece of combustion-tubing, half full of fuming hydrochloric acid. At first the heat of a water-bath is sufficient, but after a few hours the temperature is gradually raised to 140° or 150° C. The ore is completely decomposed in four or five hours, and after the tube has cooled the end may be broken under water, and the ferrous oxide at once estimated by bichromate. The same method will yield a solution suitable for the determination of the other constituents of the ore.

Reduction of Sesqui-Salts of Iron to Proto-Salts.

Sulphurous acid or metallic zinc is the reducing agent usually employed, but a much more effectual and rapid agent has been proposed, in sulphuretted hydrogen, by Mr. Reynolds. This answers much better than either zinc or sulphurous acid. The reduction, even in a strongly acid solution, takes place immediately ; and on boiling until the sulphuretted hydrogen is expelled, the sulphur separated coagulates completely ; so that, after allowing the solution to cool in the flask in which it has been boiled, a cork being placed in the neck during the cooling, filtration may be effected so rapidly that no oxidation need be feared, and the determination may then be effected with permanganate, as usual. It is better to add a considerable quantity of water to the solution before reduction, to avoid the oxidation which would afterwards ensue in the filtration of a concentrated solution of iron protoxide.

Gravimetric Estimation of Iron.

Mr. C. F. Cross calls attention to the following facts in connection with this subject:—

(1.) That ferric oxide, when precipitated in presence of salts of the fixed alkalies removes a certain quantity of the latter from solutions, this quantity being within certain limits independent of the amount of alkaline salt present in solution, but varying with the temperature of the solution at the time of precipitation, being much greater in the case of cold than of hot solutions.

(2.) That the error due to the retention of alkaline salt may, by persistent washing with boiling water, be reduced to a minimum, but not completely eliminated.

(3.) That the error is very much greater when the oxide is precipitated by excess of alkali in presence of salts of the alkaline earths; but that the latter may be effectually separated from iron by precipitating this metal in the form of the basic acetate.

(4.) That ferrous sulphide does not exert this adhesive action upon salts in solution, and is therefore, where the circumstances of the analysis permit, the best form in which to separate iron from the other metals which accompany it.

Volumetric Estimation of Iron by Sodium Thiosulphate.

M. Mohr has shown that the direct estimation of iron perchloride, by means of a solution of sodium thiosulphate, does not give satisfactory results. The cause of error lies chiefly in the decomposing action exercised by free hydrochloric or thiosulphuric acid.

By using sufficiently diluted acetic instead of hydrochloric acid, or by treating the weak hydrochloric solution by sodium acetate, it will be found that the thiosulphuric acid is not decomposed, even after some length of time. Consequently, a solution of iron perchloride may be estimated by means of a thiosulphate solution, taking care to add previously sufficient sodium acetate to make apparent the red colour of the ferric acetate, and then sufficient weak hydrochloric acid to make this colour again disappear. Then pour into the solution a known quantity of thiosulphate, and estimate the excess of this reagent which colours the liquid a deep violet, by means of starch paste and iodine solution.

Very exact results are obtained in this way; but care must be taken to use liquids not too much diluted; 0.00012 gramme is the minimum amount of iron which should be contained in one c.c.

One equivalent of iron perchloride exactly decomposes two equivalents of sodium thiosulphate.

Volumetric Estimation of Iron with Copper Subchloride.

Copper subchloride has been found by Dr. Winkler to be a very powerful reducing agent for iron sesquioxide, analogous to tin protochloride in its effects. But whilst tin protochloride causes but a partial reduction in a cold solution, copper subchloride acts directly with theoretical accuracy at the lowest temperature, and at any dilution. It is, therefore, particularly adapted for the volumetric determination of iron. The completion of the reduction may be ascertained with certainty by the addition of a few drops of potassium sulphocyanide to the solution to be tested, when the well-known deep-red colour appears. When the subchloride solution is dropped into one of iron so coloured, the red colour becomes lighter and lighter, and finally disappears entirely. After the solution is bleached, the reduction of the iron is complete, and the next drop of copper solution causes a precipitation of copper subsulphocyanide. This gives a double indication of the end of the reduction, namely, the bleaching of the red colour of the iron sulphocyanide, and the cloudiness produced by the insoluble copper salt. The rapidity and simplicity of the process, as well as the few accessories required, especially recommend this method to technical laboratories, where the want of a short and accurate process has long been felt.

The Solution of Copper Subchloride is made by dissolving sheet-copper in nitric acid; evaporate, to drive off the excess of nitric acid; and dissolve the residue in water containing hydrochloric acid. This solution is put into a flask, and a quantity of common salt equal in weight to the residue of dry copper-salt is added, in order to prevent the separation of a precipitate of copper subchloride during the subsequent reduction. Several pieces of sheet-copper are put in the flask, and the liquid is then heated to boiling. This is continued until the solution is nearly colourless, and all the copper chloride has been changed to subchloride. The flask is then corked, and allowed to cool; the solution is then diluted with water containing hydrochloric acid, until 1 c.c. corresponds to 6 milligrammes of iron. In order to keep this solution without change for further use, it should be poured into a bottle, to which is fitted an air-tight stopper, and containing a spiral of thick copper wire reaching from the bottom to nearly the neck. This completely protects the copper subchloride from oxidation, so that the strength of the solution remains nearly always the same. It is, however, best to determine the strength of the standard from time to time, since this requires but a few minutes. For this purpose, there is needed a—

Solution of Iron Sesquichloride of known strength. This may be made, according to Fresenius, by dissolving in hydrochloric acid and potassium chlorate 10.08 grammes of piano-wire, corresponding to 10.0 grammes of pure iron, and diluting to 1 litre. For each

test of the standard 10 c.c. of this solution are taken, containing 100 milligrammes of iron.

In performing this volumetric determination of iron, there are but few rules to be observed. It is advisable that the solution to be treated be decidedly acid, and very dilute before it is brought under the burette. A solution that contains from 100 to 200 milligrammes of iron should be diluted to 500 c.c. or more.

In noting the end of the reduction, though it is not necessary that the solution of potassium sulphocyanide should contain a known amount of this salt, yet it will be found better to use about the same strength at all times, since the presence of too much sulphocyanide makes the reaction less marked.

In adding the sulphocyanide, care must also be taken; for, if too much is added to the iron solution, although a deeper blood-red will be obtained, yet a difficultly-soluble copper subsulphocyanide may separate, clouding the solution and redissolving with trouble. Four or five drops of solution are quite sufficient to be added. Then, by dropping in the copper solution, the bleaching takes place with extraordinary sharpness, and only when all the iron has become a protoxide does the next drop cause a permanent cloudiness.

The presence of coloured metallic compounds (such as cobalt, nickel, and copper salts) does not in the least hinder the recognition of the reactions, if the solution is properly dilute. Neither does the presence of arsenic acid affect the process, since this is not reduced by copper subchloride. This process, therefore, is important to the metallurgist, who is often compelled to determine quickly and correctly the amount of iron contained in a matt, or speiss, or other product. By the above process this is possible in an hour.

Volumetric Estimation of Iron with Potassium Permanganate.

J. Krutwig and A. Cochetoux find that the permanganate process (Margueritte's) may be safely used in presence of hydrochloric acid if the following precautions are observed:—

1. If possible, dissolve the ore in very little sulphuric acid.
2. Reduce by means of zinc in the hydrochloric solution.
3. Add a quantity of sulphuric acid twice as great as that of the hydrochloric acid.
4. Dilute the solution to about 300 c.c.
5. Use dilute permanganate in titration.

To ensure accuracy in this estimation, M. Moyaux has drawn up certain memoranda which deserve attention in order to secure uniformity of result. The titration of the permanganate solution can only be properly made by means of metallic iron, and, when the latter metal, in a sufficiently pure state for this purpose, is not at hand, oxalic acid should be employed. The use of iron ammonio-sulphate for obtaining the standard should be rejected. Unless the precise

composition of this salt is repeatedly ascertained, it is not to be relied on, and this testing is a loss of time. The evaporation of solutions of iron containing hydrochloric or other volatile acids, after the addition of sulphuric acid, always impairs the result of the titration. The reduction of solutions of iron per-salts to proto-salts, after driving off excess of hydrochloric acid, is best effected by amalgamated zinc if zinc is used at all, but this last metal is to be rejected when a solution of iron happens to contain, at the same time, a proto- and a per-salt. When 0.8 gramme of ore is taken for assay, in case the ore contains more than 40 per cent. of metallic iron (or, when less than that quantity, 0.5 gramme is taken for assay), the quantity of fluid best suited to yield accurate results should not, in either of these cases, respectively exceed $\frac{1}{4}$ or $\frac{1}{2}$ a litre.

Mr. E. Hart considers that by far the best method of estimating iron volumetrically is by potassium permanganate after previous reduction of the ferric to a ferrous compound. The difficulty encountered is how to perform this reduction in the best, quickest, and cheapest manner. The best and most complete method of reduction is that by hydrogen, in a porcelain tube, at a red heat. To make the reduction complete it is necessary to pass the gas over the heated ore for three hours. Not more than 0.8 gramme of the ore should be taken, otherwise at the end of the time specified the reduction will be found to be incomplete. The ore is weighed out in platinum boats, four of which may be placed in the tube and reduced at once. The tube is allowed to cool while the hydrogen is still passing, the boats removed, and carefully dropped into flasks containing hot dilute sulphuric acid. The flasks are closed with doubly-perforated corks, and a current of hydrogen is passed into them while the iron is dissolving. When the solution is complete the flasks are plunged into cold water (hydrogen being still passed into them) and allowed to cool completely, and are then titrated in the usual way. Coal-gas cannot be used in place of the hydrogen, as some of its constituents dissolve in the hot acid and exercise a reducing action on the permanganate. With a great many ores, especially limonites, the reduced iron dissolves with great difficulty, sometimes not at all. This difficulty has been overcome by Dr. T. N. Drown, who passes oxygen or air over the heated ore for half an hour before reducing. The carbonaceous matter is in this way destroyed, and the reduced iron is found to dissolve with the greatest ease.

Almost all the magnetites when dissolved in acid leave a residue containing iron. The iron in this residue is not reduced by the hydrogen when the iron is determined as above. In this respect, however, the process is neither better nor worse than those ordinarily used. There are only two valid objections against this method. The first is, the gas consumed, which makes it costly; the second, the time required—from four to six hours.

To estimate iron very rapidly, with a reasonable degree of accuracy, no process has given better results than that by reduction of the hydrochloric solution of the ore by stannous chloride. The ore is dissolved in hydrochloric acid in a beaker, and evaporated nearly to dryness. The solution is then diluted with a little water, and an excess of stannous chloride run in from a burette. After the fluid has lost colour a little starch solution is added, and iodine solution run in from another burette until the blue iodide of starch remains permanent. It is found best to have the iron solution rather concentrated and warm. One c.c. of the stannous chloride solution is equivalent to about 0.012 metallic iron and 3 c.c. of iodine solution. The stannous chloride works best when freshly prepared.

Four samples have been weighed, dissolved, reduced, and titrated in an hour and twenty minutes. In a second trial, with four more samples, the same time was taken. In both cases the solutions were standardised while the ore was dissolving. This gives an average of twenty minutes as required for one determination, which is all that could be desired. It is best to standardise the stannous chloride solution by means of metallic iron. This is dissolved in hydrochloric acid and a few pieces of potassium chlorate added; after which the solution is evaporated nearly to dryness. By this means every trace of free chlorine seems to be expelled. A solution of ferric chloride, when freshly prepared, is reduced almost immediately upon addition of the stannous chloride. After standing some time, however, it is more slowly reduced, and seems to require less tin solution.

Messrs. W. F. Stock and W. E. Jack make the following remarks on the working of the stannous chloride process. They find certain objections presenting themselves—viz. the fear of adding excess of stannous salt, and the want of suitable means to prevent such excessive addition; but by the method of use given below, these objections no longer hold good.

In this process 1 gramme of ore is dissolved in 80 c.c. of strong hydrochloric acid, and, if not decomposed by hydrochloric acid, it is first fused with alkaline carbonate, and brought into hydrochloric acid solution; in either case, the solution is made up to 500 c.c. with distilled water and caused to boil. The stannous chloride may now be added in small portions at a time, but it *must* be in *dilute clear acid* solution, a convenient strength containing 10 grammes of tin per litre. The colour of the ferric solution is a fair guide to the addition of the tin-salt within certain limits; but when the colour becomes faint some other indicator must be used, and this we find in a dilute, recently-prepared solution of potassium sulphocyanide, which is disposed in drops over the surface of a white tile. Special care must be taken to add the trial drops of iron solution quickly to those on the tile, and to have the beaker containing the solution in pretty close proximity to the tile, so as to guard against oxidation of solution on the glass rod with which

the test drops are added. The reduction is carried so far that only a faint tinge of pink is produced when the last addition of tin-salt has been made and allowed to boil for a few moments. The next step is the titration with potassium bichromate; and, as a vital part of the process, make the preliminary addition of three drops of bichromate (standard solution 1 c.c.=0.01 gramme iron), then test with potassium sulphocyanate. A distinct access of colour in this test, as compared with the last test made in reducing, is accepted as proof of the absence of stannous salt, and it only remains to complete the assay in the usual manner.

M. A. Eilmann points out that coaly matter and iron sulphide act during the estimation like iron proto-salts and cause high results. Massive iron pyrites is only slightly decomposed, but it is very probable that the form of pyrites doubtless occurring in iron ores, similar to coal brasses, is attacked by acid solutions of iron perchloride at the boiling temperature. All alkaline and earthy sulphides, most varieties of iron sulphide, zinc, lead, cadmium, &c. sulphides, and, difficultly, copper sulphides are decomposed in this manner.

If we boil the finely-powdered iron-stone with *dilute* hydrochloric acid, *invariably* filter off the insoluble matter, and determine the iron by the bichromate method in a solution nearly warm, and not boiling, all difficulties vanish. A fresh portion, calcined, and fused with potassium bisulphate, gives the total iron in a soluble form to hydrochloric acid. It is invariably found that fusion with bisulphate is capable of freeing siliceous matters from iron in less time and at lower temperatures than fusion with alkaline carbonates.

Reduction of iron peroxide by stannous chloride seems objectionable where there is organic matter present. In the first place it must be done in a highly concentrated acid solution, when each drop taken out to ascertain the progress of the reduction represents a notable quantity of the substance under examination; and secondly, it is difficult to remove excess of the reducer. A much more preferable plan is the addition of ammonia and ammonium sulphide in excess, then ebullition with excess of hydrochloric acid to expel the sulphuretted hydrogen, then filtration from sulphur. This does not take a long time, and is very exact.

Titration of the iron by bichromate at the boiling temperature is quite unnecessary if a little time is allowed for the reaction; if the temperature be not high the oxidation seems to take an appreciable time, and may therefore lead to a false estimation. A cold solution may indeed be used, if the final reactions be not too hurriedly noted, while at a warm temperature the organic matter dissolved from the coaly matter of an ironstone does not interfere.

New Methods of Estimating Iron and Alkalies Volumetrically.

These methods, devised by M. P. Charpentier, are based on the employment of alkaline sulphocyanides, and on the well-known reaction ensuing when they are brought in contact with a iron per-salt. If, into the red liquid formed by adding a solution of an alkaline sulphocyanide to a solution of an iron per-salt, there be poured a caustic alkali, the red colour disappears, iron peroxide is thrown down, the alkaline sulphocyanide being reconstituted. Other things being equal, it is necessary to add so much the more alkali the more iron there is in the original solution. To titrate the alkaline liquid employed in the operation, dissolve 5 decigrammes of pure iron in very dilute hydrochloric acid. It is very important that this solution is exempt from free acid, and that all the iron is in the state of sesquioxide, the latter condition being attained better by means of potassium chlorate than of nitric acid. This solution is diluted with water to the volume of a litre. Of this, 100 c.c. are placed in a white porcelain capsule, and a few drops of potassium sulphocyanide are added, when the liquid takes a deep blood-red colour. By means of a graduated burette, caustic potash is then added, of such a strength that about a buretteful would be required to saturate a litre of the iron solution. The red liquid becomes gradually turbid, and then suddenly grows colourless, whilst the iron sesquioxide is precipitated. The amount of alkali consumed is read off. The same alkali is then used to titrate the remaining 900 c.c. of iron solution. The number of degrees, increased by 1.9th, is the strength of the alkali sought for. These points being arranged, in order to analyse any ferruginous matter—whether ore, slag, or mineral water—a neutral solution in water or hydrochloric acid is prepared, diluted to a litre, and, after the addition of potassium sulphocyanide, is titrated as above. If the number of degrees found is N' , then $\frac{N'}{N}$ is the proportion of iron in the body under examination,

N being the number of degrees of alkali required for the standard iron solution. In case of a mixture of sesquioxide and protoxide, commence by determining the pre-existing sesquioxide as above, avoiding contact with air, and adding ammonium chloride to hinder the precipitation of iron protoxide. A second portion is then perfectly peroxidised, and the total iron is determined. The difference shows the amount of protoxide. In this case, it is advantageous to replace the potash with ammonia. If desired, the iron solution may also be poured into a known and fixed amount of alkali, mixed with sulphocyanide. The appearance, not the disappearance, of the red colour is here decisive. After the application of this method to any given sample, the analysis can, if required, be completed by the ordinary gravimetric method. If the substance under examination contains substances precipitable by ammonia, and this alkali is employed, their precipitation may be hindered by means

of ammonium chloride; such substances are—Lithia, baryta, strontia, lime, magnesia; the manganese, iron, zinc, and cobalt protoxides; cadmium, silver, platinum, rhodium, osmium, and ruthenium oxides. The following oxides are not thrown down by an excess of potash:—Lithia, baryta, strontia, alumina, glucina, and zinc, chrome, lead, platinum, tin, palladium, rhodium, osmium, and gold oxides. In this case, potash is employed as the standard alkali. In most cases foreign substances do not interfere. This holds good with silica, the alkaline metals, the alkaline earths, alumina, manganese, zinc, cobalt, nickel, cadmium, chromium, lead, bismuth, silver, and all metals which give white precipitates with alkaline sulphocyanides. The application of the method to alkalimetry is based upon the following reaction:—If an excess of caustic alkali is present in a liquid along with a little iron sesquioxide recently precipitated, and if hydrochloric acid is gradually added, as soon as the alkali is saturated the iron oxide is attacked, and a ferric solution formed which immediately gives a blood-red colouration, an alkaline sulphocyanide having been added as indicator. The method is, of course, acidimetric as well as alkalimetric.

Repetition in Volumetric Analysis.

When iron is determined by means of potassium permanganate, all the iron is, at the end of the operation, in the form of sesquioxide, while there is also a very small excess of unreduced permanganate. Mr. Bryant Godwin proposes that, as a control, the solution should be boiled for a short time with pure zinc-dust, and rapidly filtered and washed with water (previously boiled to expel air). This reduces the iron again to ferrous oxide, and the process of titration may be repeated a second, and even many more, times, until the bulk of the liquid becomes too large to handle.

Estimation of Carbon in Iron and Steel.

This is a problem of considerable difficulty, and to secure accurate results many special precautions are necessary, owing to the large preponderance of the iron over the carbon present. The carbon may be present in two forms—as combined carbon, and as free or graphitic carbon. The estimation may be of the total carbon present, or of either the combined or graphitic separately, and the method of analysis adopted will have to be selected accordingly. The following is a description of the most satisfactory processes which have been devised for these estimations.

A. Estimation of the Total Carbon.—Bromeis, modifying Regnault's process, treats the iron as if it were an organic substance, and burns the carbon off:—About two inches of a combustion-tube of hard Bohemian glass, closed at one end, are filled with a mixture of equal parts of lead chromate and potassium chlorate. Three grammes of the iron under examination, in a state of very fine division, are inti-

mately incorporated with 50 grammes of a mixture of 40 parts of lead chromate and 6 parts of previously-fused potassium chlorate, and introduced into the combustion-tube, and lastly a layer of lead chromate. To the tube a calcium chloride and a Liebig's potash apparatus are attached; the former to retain traces of moisture, the latter to absorb the carbonic acid formed. The combustion-tube is cautiously heated, first near the open end, as in the process of organic analysis. When the mixture of the iron with the lead salt is brought to a dull red heat, the metal burns with incandescence, and the carbon is oxidised to carbonic acid, which is absorbed by the potash solution. At the close of the operation the mixture at the extreme end of the tube is heated, oxygen is evolved, all carbonic acid is driven forward, and the last traces of carbon consumed. From the increase of weight of the potash apparatus, due to carbonic acid, the amount of carbon may be calculated. Mr. Tosh, in reporting on this process, says that the results of different experiments agree well with one another. There is reason to think, however, that the percentage of carbon indicated is somewhat too low, on account of loss of carbon during pulverisation of the iron. This loss, as pointed out by Morfit and Booth,¹ is often appreciable, and in the case of highly graphitic iron, very considerable. With this one exception, the process is in every respect commendable, and where, as with spiegeleisen or white iron, this loss of carbon cannot take place, it strongly recommends itself.

The process devised by Professor Wöhler is strongly recommended by Mr. Tosh, who has made many determinations by its means. It is carried out in the following way:—A weighed quantity of iron contained in a porcelain boat is placed in a hard glass tube, and exposed at a dull red heat to the action of chlorine (first dried by passing over pumice-stone saturated with sulphuric acid) till no more iron perchloride is formed. The whole of the carbon remains in the boat, which, when cool, is transferred into a porcelain tube, and the carbon burned in oxygen. An estimation by this method may be performed in two hours. No portion of slag should be present with the iron or the carbon in presence of silica, and chlorine at a high temperature may form carbonic acid and silicium chloride, thus leading to loss of carbon. Care must be taken to have the chlorine perfectly free from moisture, otherwise a portion of carbon may be lost by the formation of hydrocarbons. The results given by this process are very concordant. The perfect combustion of graphite, even in oxygen, requires a very high temperature. The most convenient plan is to place the graphite first in a platinum boat, insert this into a well-glazed porcelain tube, and expose to a full red heat in a small charcoal furnace. In a gentle stream of oxygen the carbon is perfectly burned in a few minutes, and the resulting carbonic acid is absorbed in the usual way by potash solution.

¹ *Chemical Gazette*, vol. xi.

Fresenius recommends that a weighed portion of the metal, in borings or chippings, be dissolved in dilute sulphuric acid by the aid of heat. The gases evolved during solution, consisting mostly of hydrogen, are passed over red-hot copper oxide. The gaseous hydrocarbons are burned, and the carbonic acid formed, after drying by calcium chloride, is absorbed by potash solution in a Liebig's apparatus, and then weighed. This only gives the combined carbon, and when an estimation of the total carbon is required, the matter remaining behind, insoluble in the dilute sulphuric acid, is collected and burned in a stream of oxygen, and from the weight of the resulting carbonic acid the amount of carbon may be deduced. This quantity, added to that obtained by burning the gases over copper oxide, gives the total quantity of carbon contained in the iron. In drying the insoluble residue previous to combustion in oxygen, an elevated temperature must be carefully avoided; in fact, the safest way is to dry over sulphuric acid. The presence of hydrocarbons in the graphitic residue shows that this process cannot be safely applied for the estimation of combined carbon directly.

Weyl's very ingenious method for the estimation of the total carbon is founded upon the fact that a piece of iron, attached to the positive pole of a galvanic battery, and suspended in hydrochloric acid, is dissolved, while the hydrogen is given off at the negative pole. The formation of hydrocarbons, and consequent loss, is in this manner prevented. One great advantage in this method is that the iron does not require to be in powder. A piece of iron 2 to 4 grammes in weight, attached to the positive pole of a Bunsen's cell, is suspended in dilute hydrochloric acid, just below the surface of the liquid. From the negative pole hydrogen passes off, while the iron dissolves quite quietly, and the strong solution of iron protochloride formed may be seen falling in a regular stream through the lighter liquid. The iron is dissolved in about twenty-four hours, and the carbon is left behind in the same shape as the piece of metal from which it was derived. In Weyl's earlier experiments it was found that some of the liberated carbon at the positive pole was carried over to the negative pole by the mechanical working of the stream. To prevent this, a diaphragm of bladder or parchment paper is interposed between the two, which entirely obviates the possibility of loss in this way.

Mr. Tosh uses a small platinum sieve in which to lay the pieces of iron wholly immersed in the acid, and the action proceeds to the end as well as it does at the commencement. Any interruption of the current is not to be feared, as both amorphous carbon and graphite are good conductors of electricity. In this process there is always a minute loss of carbon, owing to a slight evolution of hydrogen, which always takes place from the piece of iron during solution. This evolved hydrogen possesses the characteristic odour due to the presence of hydrocarbons, always noticeable when cast-iron is dissolved in

acids under ordinary circumstances. When no more hydrogen is given off at the negative electrode, showing that all the iron is dissolved, the carbon is collected in a small funnel stopped with asbestos, dried cautiously, transferred to a platinum boat, and burned in a stream of oxygen, and the resulting carbonic acid is absorbed in the ordinary way by potash solution.

Weyl has proposed a second method for the solution of iron without the evolution of hydrogen, which consists in suspending a piece of the metal in dilute sulphuric acid containing potassium bichromate dissolved. The carbon is unaffected, and when most of the iron is removed, the residue may be collected and burned in oxygen. Ferric chloride is capable of acting in the same manner.

The galvanic process was, we believe, first employed by Mr. Binks many years before Weyl published it. In a paper read before the Society of Arts in 1857, Mr. Binks describes a new method of analysing iron in the following words :—‘The best malleable iron, on the one hand, and by way of comparison with this, the same kind of iron fully converted by the usual process, were taken on trial ; the steel was dissolved in a very dilute and pure hydrochloric acid, and after many trials it was found best to place the bar of steel or iron in single voltaic arrangement with platinum, and to effect the solution in the cold with the usual precaution of expelling air from the water employed. In this way,* slowly, the steel was dissolved, and the carbonaceous flocculent matter that was left collected, carefully dried, and analysed. The iron was treated in the same manner, and the comparatively very small proportion of carbonaceous residue given by it also examined. And these were compared with the residue obtained also from cast-iron. If the acid be strong, and heat be used, and the voltaic arrangement be not used, the results are very different. Gaseous nitrogen, in very minute quantity, is given off along with the hydrogen, some ammonium chloride is formed in the solution, and but little nitrogen left in the residue.

Boussingault dissolves the iron by means of a solution of mercury bichloride, which transforms the iron into protochloride, without there being the least evolution of a gas capable of carrying off or uniting with the carbon. The powdered iron is mixed with fifteen parts of bichloride. Add rapidly enough water to form a thin paste, and triturate for about half an hour in an agate mortar (when there is no objection to the introduction of a little silica, a glass mortar may be used). The diluted paste is introduced into a hard glass flask, and kept for an hour at a temperature of 80° or 100° C. Then throw it on a filter and wash with warm water. The mercury protochloride containing the carbon, after being well dried in a water-oven, is put into a platinum boat and introduced into a glass tube communicating with a generator of dry hydrogen. Heat gradually up to a red heat in the current of gas. The protochloride is volatilised without decomposition. The volatilisa-

tion of the protochloride may equally well be effected in a current of nitrogen; but independent of the fact that it is not easy to keep up a sustained current of this gas, there will always be a suspicion of the presence of a little oxygen. In this respect hydrogen offers more security, especially if the device is employed of passing the dry hydrogen over a column of spongy platinum before it arrives at the tube containing the boat. The sponge retains the arsenic, and determines the disappearance of the oxygen which the hydrogen gas might contain. In proportion as the mercury protochloride disappears, the presence of carbon becomes manifest. Allow the boat to cool in a current of hydrogen, and then weigh it with the usual precautions. The carbon is voluminous, and of a fine black colour; it ignites and burns like tinder if the boat is heated a little. This is generally the case with carbon extracted from white iron, wrought-iron, and steel. The graphite coming from grey cast-iron only burns with the assistance of pure oxygen. The carbon leaves an ash after its combustion. Before weighing this residue it must be heated red-hot in a current of hydrogen. The silica of this ash, when present in steel or wrought-iron, in which it cannot be supposed to be due to scoria, comes from silicide; but it does not represent the whole of this, because the silicium in combination with the iron, being first transformed into chloride by the mercury bichloride, passes by the action of water into the state of silica, of which one part, being soluble, is carried away in the washings, while another part, insoluble, is left with the mercury protochloride. It is this insoluble silica which is found after the combustion of the carbon.

The metallic substances submitted to the action of mercury bichloride should be reduced to powder. There is no difficulty in this in the case of white cast-irons, for they pulverise easily. But when grey cast-irons, steel, and especially wrought-irons, are operated on, recourse must be had to the file to divide them, and this is an inconvenience which every one has experienced.

B. Estimation of the Graphite.—The employment of iodine and water for dissolving the iron and leaving the carbon has been recommended by some, and the weight of the carbonaceous residue obtained was thought to afford an approximate indication of the amount of carbon. But for this purpose it is necessary to dry the carbonaceous residue under the air-pump, or at a temperature of 120° to 180° C. Dr. Eggertz has shown that the quantity of carbon thus obtained is too great, though the weight of the residue is constant. He has also found that the residue contains iodine and water. To ascertain whether the quantity of carbon in the residue so obtained is uniform, he has burnt the residues from several different kinds of pig-iron and hard steel, and finds that the average amount of carbon is 59 per cent. Other analyses of the residue obtained from white pig-iron (free from

graphite) gave as a mean result, after deducting the silica, the following as the composition of the carbonaceous residue :—

Carbon	59.69
Iodine	16.07
Water	22.50
Nitrogen	0.13
Sulphur	0.23
Loss	1.38
									<hr/>
									100.00

The variation in the amount of carbon in four analyses was 0.5 per cent. The amount of carbon in the residue being taken as 60 per cent., since the quantity of this residue may vary to the extent of 1 per cent., owing to the different amount of sulphur in iron, the error in the estimation of carbon in steel containing 2 per cent. carbon would not amount to more than 0.08 per cent. The carbonaceous residue does not change in weight when heated from 95° to 110° C.; but it loses 9 per cent. by heating to 150°, and about 38 per cent. by heating to 240°. Heated for a long time in a water-bath with hydrochloric acid, its character seems to change, iodine and water being disengaged and oxygen absorbed.

Colorimetric Estimation of Carbon in Iron.

Prof. Eggertz has modified his original process so as to increase its accuracy. He remarks that when pure ferric hydrate, free from chlorine, containing 0.1 gramme iron is dissolved in 2.5 c.c. nitric acid, free from chlorine, of 1.2 sp. gr., a yellow-green solution is obtained; when put into a burette as commonly used for colorimetric carbon testing, about 12 millimetres diameter, and a further addition of 1.5 c.c. nitric acid made, it clears somewhat, but not so much as when water is added instead of nitric acid. The warm solution has a much stronger colour than the cold. Add afterwards in both cases 4 c.c. water, so that the volume of the solution amounts to 8 c.c. Note now that the iron colour has gone. It follows, as a rule, in colorimetric carbon testing, that the iron solution is to be diluted with *at least* the same quantity of water as of nitric acid used for solution, also that the volume of the solution never ought to exceed 8 c.c. when the colour is read off.

The nitric acid as well as the diluting water ought to be free from chlorine or hydrochloric acid. Whenever a very slight trace of such is present it communicates to the iron solution a yellowish colour.¹ The

¹ Only 0.0001 gramme of chlorine in a solution of 0.1 gramme of iron from ferric hydrate in 2.5 c.c. nitric acid produces a decided yellow colour. Dilute this solution with 1.5 c.c. nitric acid and 4 c.c. water, the colour is still observed, but less in proportion as the solution is diluted.

quantity of nitric acid required for solution is regulated to a certain degree by the supposed amount of carbon in the iron. Thus, employ for solution of iron with a lower amount of carbon than 0.25 per cent., only 2.5 c.c. nitric acid, with carbon of 0.8 per cent. use 8 c.c., with carbon 0.5 per cent. use 8.5 c.c., and for carbon 0.8 per cent. use 4 c.c. nitric acid. For steel with a greater amount of carbon take 5 c.c. nitric acid, as also for white cast-iron, but only 0.05 gramme of it should be weighed with great accuracy.

When the amount of carbon is altogether unknown, begin with 2.5 c.c. nitric acid, and afterwards add more as soon as the colour of the solution, or the amount of separated carbon, shows that more acid is required. A little more acid than here given does no harm, only afterwards add at least the same volume of water, and for white cast-iron 7 c.c. may be taken to prevent the quick precipitation of a humus-like substance after dilution. If too little acid has been used, the solution will have too deep a shade.

The iron to be tested must be finely divided either by filing by means of a clean and sharp file,¹ or, better, by boring or planing by means of a steel edge, for which an old three-cornered file can be adapted by grinding off the teeth and furnishing with a handle at each end; or, if very hard, crush the iron in a steel mortar.

For solution of the iron use test-tubes of about 15 millimetres diameter and 120 millimetres long; dry with clean clippings of filter-paper thickly rolled together. Transfer into the test-tube from the weighing-scoop with the help of a hair pencil the accurately-weighed amount of iron, 0.1 gramme, or, if white cast-iron, 0.05 gramme; then add 2.5 c.c. or more nitric acid of 1.2 sp. gr., and free from chlorine. The measuring of the acid can be best done by means of a small pipette, 10 millimetres diameter, graduated to whole and half cubic centimetres. The test-tube is covered with a small watch-glass (28 millimetres diameter), and it is now placed into a cylindrical copper dish, 100 millimetres deep and at least 120 millimetres diameter; upon this is placed a copper lid furnished with a thermometer tube-hole, and holes for the test-tubes, marked with numbers. The dish is previously provided with water, also some grammes of paraffin wax to hinder evaporation. Heat up the dish over a gas or spirit flame to 80°, and maintain at this temperature the whole time. Shake the tube while the iron is dissolving. Solution is ended when no gas bubbles are evolved; this may require one and a half to two hours, or sometimes more, according to the amount of carbon in the iron.

This has been the ordinary method followed hitherto, but experience has shown that the maintaining of the temperature of 80° demanded attention which could by no means be always given. It was also of

¹ Through the wearing of the file the amount of carbon in the iron can be considerably increased.

less consequence whether or no a normal solution was dissolved every time in the same manner as the iron whose carbon contents were to be estimated. But if this is to be avoided, and unchangeable normal solutions are used, the solution must be always made at the same temperature, and to this end it is safer to place the test-tube in boiling water. By this method the time for solution is shortened to about three-quarters of an hour, and the colour of the solution will be a little stronger than by dissolving at 80°. If an occasional necessity calls for still greater speed, the solution can be made in about a quarter of an hour by means of gentle boiling over a lamp flame, between which and the test-tube a suitable brass wire gauze is placed, on which the tube may rest, but the colour of this solution will commonly be a little darker than when using the temperature of 100°. The reason for employing 80° instead of 100° was, that at the latter temperature a reddish-yellow sublimate-like film was obtained in the tube, which afterwards came into the solution and made it dim. When such happens, try to dissolve the film in the solution by violent shaking, and if this is not successful, filter it off. The film is composed only of nitric acid and ferric oxide, as it appears in heating pure ferric hydrate in nitric acid.

As soon as all evolution of gas ceases, take out the test-tube and place it in a beaker with water to cool, when it ought to be covered with a cap of pasteboard to protect it from daylight, by which the solution is soon bleached. When protected from light in this manner the solution maintains its colour for several days. The burettes employed for carbon estimations ought to have a volume of 80 c.c., and be graduated in $\frac{1}{10}$ c.c. and furnished with an opening and spout. The solution is then placed in the burette, which may be done through the filter. If the solution is not clear, or graphite is present, at least an equal amount of distilled water (including the wash-water from the test-tube used for boiling) must be added to the nitric acid used, and the volume made up to at least 8 c.c. before comparison with the normal solution.

The normal steel is prepared in like manner, and diluted with so much water that every c.c. of it corresponds to 0.1 per cent. carbon; this can afterwards, by careful dilution with water, be made of such strength that every c.c. corresponds to 0.05, 0.02, 0.01, or 0.005 per cent. carbon in 0.1 gramme iron. Of normal steel with, for example, 0.80 per cent. carbon, dissolve 0.1 gramme in 4 c.c. nitric acid, and dilute with water to 8 c.c. Mix carefully after every dilution, because the lower strata of the solution will otherwise be of too deep a colour. Before reading off (which is done from the upper edge of the solution) allow it at least one minute to flow down from the sides of the burette.

The above-named special normal solution can be marked and employed as follows :—

Solutions	Carbon per cent. per c.c. of 0.1 gramme of Iron	Used for Iron with Carbon per cent.
Normal . . .	0.10	0.8 and higher
$\frac{1}{2}$ N . . .	0.05	0.4 to 0.8
1.5th N . . .	0.02	0.16 to 0.5
1.10th N . . .	0.01	0.08 to 0.25
1.20th N . . .	0.005	0.04 to 0.08

The lowest amount of carbon found in any iron is 0.04 per cent., and in employing the last-named normal solution, good daylight is required: this is also best for all colorimetric testing.

Greater dilution than '20 times cannot be used in common burettes of about 12 millimetres diameter, but by using tubes of 24 millimetres diameter, the difference is well marked between a 40-times diluted normal solution and distilled water, and in this way approximate estimation ought to be made of carbon in iron of about 0.02 per cent. in the case of iron so poor in carbon being produced. Measure in a small pipette 1 c.c. normal solution, dilute to 40 c.c. corresponding to 0.0025 per cent. carbon per c.c.; introduce this into a 24-millimetre test-tube, which accurately agrees with another graduated tube, in which 0.4 gramme iron is dissolved in 10 c.c. nitric acid, and diluted with water first to 32 c.c., and then, further, till their colours agree. Should such happen, for example, when the volume of the solution is 35 c.c., the amount of carbon in the iron will be $0.0025 \times 35 : 4 = 0.022$ per cent.¹

In comparing the solutions with each other by the method hitherto commonly used, in which a thin paper-filter is held behind the tube, it has been seen that much depends on the distribution of the light in the apartment, and that a room with only one window is best. Before most eyes it is seen, however, that the tube held on the right is a little weaker in colour than that placed on the left; therefore, as also prescribed from the first, the burette containing the assay should always be held in like manner, or to the right. That we may be more independent of the nature of the room, and equalise the difference in colour caused by placing the tubes to the right or left, a little camera may here be used with great advantage, in which the tubes are placed. This is made of deal 6 millimetres thick, in the form of a box open in both ends, blackened inside. The height inside is 80 millimetres, the breadth in front 26 millimetres, at the back 120 millimetres. The front of the upper side is cut out to insert the tubes, and these are kept in their places by means of a brass wire fixed in the upper front edge; also by a little trough of sheet copper on the lower outer edge. The opening is covered with a thin filter-paper fastened with a pin.²

¹ By means of the iodine method, in a sample of 8 grammes of Lancashire hearth iron, 0.038 per cent. carbon was obtained.

² The wide opening of the camera can, if desired, be covered by a screen, in

The burette and test-tube must, in respect to the quality of the glass, agree exactly in colour, and be dried outside with clean cloth before placing in the camera.

As normal steel and normal iron, two sorts made by the Bessemer process have been used lately, one adopted with 0.80 and the other with 0.16 per cent. carbon. The size is 12 millimetres square, and testing shavings are always taken at right angles to its length. The carbon has been estimated by the iodine method as described in *Jern Kontorets Annaler*, 1862, p. 47, and 5 grammes taken for every testing. From this steel three estimations gave 0.79, 0.80, and 0.82 per cent. carbon, and from the iron 0.16 was obtained in two closely-agreeing estimations. These carbon estimations have also agreed with the combustion analyses executed by Dr. A. Tamm in iron and steel with the nearest comparable amounts of carbon, as mentioned in the *Jern Kontorets Annaler*, 1874. Instead of immediately employing iodine, as was done at first, and in view of the difficulty of obtaining it pure, for these estimations iodine dissolved in iron iodide has been used. This solution is prepared by adding to a solution of 10 grammes of iron in 50 grammes iodine, further 50 grammes iodine, in which it is quickly dissolved, then filter the solution into a measure, pass water through the filter till the volume is 100 c.c. One gramme iron requires 10 c.c. of this solution. In consequence of the loss of weight in treating filter-paper with acids, platinum filters have been used to take up the carbon mass; but it is difficult to obtain them good. It appears that inconvenience is removed by using filter-paper treated with hydrochloric acid and hydrofluoric acid (see *Fresenius Zeitschrift*, 1879, p. 582), by which the inorganic components are nearly completely extracted. One of these filters, 60 millimetres diameter, gave less than 0.0001 gramme ash. Drying of the carbon mass is safest done in a water-bath at a temperature of 95° to 98°, wherein the crucible is placed in a test-tube of about 180 millimetres long and 35 millimetres diameter; the open end is closed with a cork through which passes a thermometer. By means of a bent brass wire the crucible can be inserted and drawn out.

With white cast-iron the colorimetric method has given better results than could at first be expected (see *Jern Kontorets Annaler*, 1874, p. 177), when only 0.05 is taken for testing, yet the solution must be diluted to a larger volume, whereby a little error in observation in respect to the colour will have a great influence. These solutions ought to be quickly read off, because they soon become a little dim from a humus-like substance which precipitates. By using for solution 7 instead of 5 c.c. nitric acid this inconvenience is lessened.

The different nature of the carbon, such as the so-called cement carbon, and hardening carbon has not made itself known in any other way in colorimetric testing than that the colour of the solution of the

the centre of which is placed a suitable convex or concave glass of about 40 millimetres diameter.

latter is less than the former, so that a steel of 0·8 per cent. carbon, after strongly hardening and pulverising, gives only 0·55 per cent. After heating the hardened steel to a brown heat, the original amount of carbon is again found. By the iodine process, on 5 grammes of the hardened steel 0·8 per cent. carbon was obtained. Iron with 0·8 per cent. carbon, reduced by cold hammering from 12 to 16 millimetres thickness, showed the same amount of carbon.

During solution the various sorts of iron behave with so wide a difference that the solution will sometimes be coloured instantly, at other times only after a little warming. The final colour after dilution with water will usually agree very well with the colour of the normal solution. Should any little inequality of colour remain (such as approaching to yellow or brown), less regard ought to be fixed on it than on the intensity of the colour, or on the distinctness with which the small inequalities in the paper held behind the test-tubes can be seen. From the nature of the case it follows that individuals with more or less good eyesight are found to perform these tests with more or less sharpness, but experience has also shown that the ability to see in this respect can be considerably improved by practice, and at most only few persons have found it impossible to do this work.

With reference to the presence of foreign substances in iron, and their influence upon the colour of the solution, the following experiments have been made :—

Manganese, 0·05 gramme, in the form of carbonate, dissolved in 2·5 and in 5 c.c. nitric acid with a brown colour, from the presence of a little manganese oxide. Heating to 100° produced a little precipitate (probably from hydrate of manganese peroxide), thereafter the solution had only a weak red-violet colour, which on diluting with water to 8 or 10 c.c. could be regarded as vanished. It seems from this that the colorimetric method would be serviceable for the estimation of the amount of carbon in ferro-manganese. One sample of such with about 80 per cent. manganese showed carbon approximately 4 per cent.

Phosphorus, 0·001 gramme in the form of soda phosphate added to a solution of 0·1 gramme iron as ferric hydrate in 2·5 c.c. nitric acid and 2·5 c.c. water, showed no difference in colour with a similar solution without phosphorus. Iron with 5 per cent. phosphorus is difficultly soluble, and with 10 per cent. phosphorus insoluble in nitric acid.

Sulphur, 0·001 gramme in the form of magnesium sulphate, added to 0·1 gramme iron, dissolved in 2·5 c.c. nitric acid and 2·5 c.c. water, was without influence.

0·01 gramme manganese, 0·01 gramme phosphorus, and 0·001 gramme sulphur (all in the forms given above), added to a solution of 0·1 gramme iron as ferric hydrate in 5 c.c. nitric acid and 5 c.c. water, showed no colour. The same quantities added to 0·1 gramme normal steel with 0·8 per cent. carbon, dissolved as usual, made no change in the solution or in its colour.

Copper, 0·001 gramme, dissolved in 2·5 c.c. nitric acid and 2·5 c.c. water, gave no colour to the solution.

Silicon in iron dissolves to a considerable amount in nitric acid on warming, and particles of silica begin to appear in the solution. 0·4 per cent. silicon in steel has at least not shown any influence in colorimetric testing. In cast-iron rich in silicon, graphite is always present, and must, with possibly the insoluble silica, be filtered off.

Tungsten becomes tungstic acid on dissolving the iron; it is then insoluble and must be filtered off.

Chromium, 0·002 gramme in the form of chromic hydrate, dissolved in 2·5 c.c. nitric acid and 2·5 c.c. water, gives to the solution a greyish-blue colour, which on dilution with water to double its volume is less noticeable. On greater dilution the colour diminishes, and when diluted to 40 c.c. may be said to disappear. Iron containing much chromium is difficultly soluble, or even insoluble, in nitric acid.

Vanadium, 0·001 gramme in the form of vanadic acid, dissolved in 2·5 c.c. nitric acid, gives to the solution a weak yellowish colour, which disappears on addition of 2·5 c.c. water.

Nickel, 0·001 gramme, dissolved in 2·5 c.c. nitric acid, gives a green colour on solution, which is still apparent on addition of 2·5 c.c. water, but can be regarded as absent on diluting to 8 or 10 c.c.

Cobalt, 0·001 gramme, dissolved in 2·5 c.c. nitric acid, gives, as is well known, a red-coloured solution, which is little noticeable on dilution with water to 24 c.c., but scarcely can be regarded as absent before dilution to 40 c.c.

In 1862, Dr. Eggertz showed the desirability of obtaining from inorganic substances unchangeable normal solutions, instead of those of burnt sugar in spirit, which bleached with time, and this the quicker in proportion as they were more often exposed to sunlight. Several proposals with this object have been brought forward, in which iron, cobalt, and nickel salts, potassium bichromate, &c., have been recommended. After experimenting with several such mixtures, the author, upon the suggestion of Prof. F. L. Ekman, tried chlorides of iron, cobalt, and copper, which give the best results, because with them we can, as desired, produce colour tones in yellow, brown, and green. Such mixtures, diluted with water containing 0·5 per cent. hydrochloric acid of 1·12 sp. gr., have been found stable, even after standing a long time in sunlight. By only adding hydrochloric acid in drops the mixture is strongly drawn towards yellow. From the neutral chlorides, by adding water containing 1·5 per cent. hydrochloric acid for ferric chloride, and 0·5 per cent. for both the other salts, solutions can be prepared of such strength that they contained 0·01 gramme metal per c.c. Then taking of these solutions, 8 c.c. iron solution, 6 c.c. cobalt solution, 8 c.c. copper solution, and about 5 c.c. water containing 0·5 per cent. hydrochloric acid, a mixture has been obtained of a colour entirely similar to a solution in dilute nitric acid,

of iron containing carbon corresponding to 0.1 per cent. per c.c. This solution can afterwards be diluted with water containing 0.5 per cent. hydrochloric acid to whatever normal colour is desired, and the water added in the nearest proportion with the amount of carbon. It may be necessary to bear in mind that the weights of 0.1 and 0.05 gramme for weighing off the iron must be very accurate when such artificial normal solutions are used.

Now that unchangeable normal solutions can be obtained, the time may now be come for those desiring such to apply the old method used for copper estimation in ammonia solutions, as adopted by J. B. Britton, of Philadelphia, for colorimetric carbon estimations in iron.¹ He employed a number of tubes alike in size, containing equal volumes of normal solutions of different strength, and dissolved the iron in a similar tube, and diluted with water to the same volume as the normal solutions. By comparison with these he can at once tell the amount of carbon, and thus avoid the inconvenience of the successive dilutions. Mr. Britton uses fifteen separate normal solutions for carbon amounts between 0.02 and 0.8 per cent., and he says by taking 1 to 2 grammes iron for estimation the carbon can be determined to an accuracy of 0.01 per cent. He uses for his normal solutions roasted coffee, which he found better than burnt sugar.

A greater exactness in colorimetric carbon estimations may be gained by observing the solutions in the tube from above instead of from the side; but for this purpose it is necessary that the tubes completely correspond at the bottom, that they are obtained suitably clear, and that the depth in all the tubes is alike.

By these observations the difficulties which sometimes appeared in colorimetric carbon estimations, both here and elsewhere, may be in some degree removed. At the same time it ought to be remembered that the essential properties of iron and steel do not exclusively depend on the amount of carbon.

Mr. Tosh gives the following process for the estimation of graphite:—2 to 3 grammes of iron are treated with dilute hydrochloric acid, and when the solution approaches completion a considerable quantity of strong acid is added to separate the last portions of iron and manganese. The insoluble matter, consisting mostly of graphite, is collected on a carefully-weighed filter, washed with hot water, dilute hydrochloric acid, solution of caustic soda, and hot water again, successively, and lastly with alcohol and ether to remove oily hydrocarbons. (By washing with dilute acid and with alkali, the iron and silica or silicon oxide are separated). After drying at 120° C., the filter and graphite are weighed and burned away. The small residue (a mere trace of silica or titanitic acid) is weighed, and this weight subtracted from the first gives the amount of graphite. The results obtained agree very closely.

¹ *Chemical News*, Aug. 26, 1870, vol. xxii. p. 101.

In washing the graphite with solution of soda, there is always a brisk effervescence, due to the oxidation of silicon oxide to silicic acid, by decomposition of water, with consequent liberation of hydrogen.

C. Estimation of Combined Carbon.—When steel, or pig-iron containing carbon in chemical combination, is dissolved in nitric acid, a soluble brown colouring matter is formed, whose colouring power is very intense, and the solution assumes a tint which is dark in proportion to the quantity of the chemically-combined carbon. Iron and graphite (or free carbon) do not influence this colouration; for the solution of iron nitrate is colourless, or, at most, slightly greenish, unless extremely concentrated, and graphite is insoluble in nitric acid.

Thus, in dissolving two pieces of different steels of the same weight in nitric acid, taking care to dilute the darker solution until the two liquids present exactly the same colour, it is very evident that the more highly carburetted steel will furnish the larger quantity of liquid, and that the proportion of the volumes will indicate the relative proportion of colour in the two steels. If now the composition and contents of carbon of one of the steels are known, the absolute percentage of carbon in the other steel may be immediately deduced. Dr. Eggertz has applied these reactions to a method of estimating the combined carbon.

Several modifications of this method have been proposed. The most successful of them, affording exceedingly accurate results, was communicated to the *Journal of the Franklin Institute* for May, 1870, by J. Blodget Britton, and has been tested for a considerable time. Instead of a single tube, containing a standard solution for comparison, as suggested by Eggertz, a number of tubes having their solutions differently standardised, one from the other, are employed. These are arranged securely in a wooden frame, with spaces between for placing the tube containing the solution to be tested, and forming together a convenient portable instrument called a colorimeter—a representation of such an instrument being shown in the annexed cut. The position of the tube containing the solution to be tested is shown at A. The tubes are $\frac{5}{8}$ of an inch in diameter, and $8\frac{1}{2}$ inches in length, filled with water and alcohol coloured with roasted coffee, and hermetically sealed. The solution in the tube to the left has its colour to correspond exactly with one produced by 1 gramme of iron containing 0.02 per cent. of combined carbon, dissolved in 15 c.c. of nitric acid. The solution in the tube next to it has its colour to correspond with one produced by the same quantity of iron, but containing 0.04 per cent. of combined carbon, and so with each of the other tubes, increasing 0.02 per cent. of carbon in regular succession to the right, the last reaching 0.8 per cent., as indicated by the figures on the upper rail of the instrument. On the back of the instrument, and for the purpose of partially screening the light and allowing the different shades of colour to be distinctly discerned, there is tightly stretched between the rails some fine white parchment paper. This screen is not

shown by the cut, but it serves a very important purpose. The process is conducted as follows :—1 gramme of the finely-divided metal is put into a tube of about $1\frac{1}{2}$ inch in diameter and 10 inches long, and digested for 15 or 20 minutes in 10 c.c. of nitric acid of a little more than 1.20 sp. gr., free from chlorine. The solution is then cautiously poured into a beaker, and a small portion of metal, which remains undissolved and adheres to the bottom of the tube, is treated with 5 c.c. of fresh acid, exposed to a gentle heat till completely dissolved, and added to the other. The contents of the beaker, when sufficiently cool, are filtered through two thicknesses of German paper (not previously moistened, and of a diameter not exceeding $4\frac{1}{2}$ inches) into a tube about 5 inches long and of precisely the same diameter as those in the instrument. After the filtered solution has remained for some minutes at the temperature of the atmosphere, and its colour become fixed, the tube is placed in the instrument and the carbon



FIG. 3.

determined by a comparison of shades ; the determination may be made readily as close as 0.01 per cent. Heat should not be applied in the first instance to facilitate the solution of the metal, because a high temperature is apt to cause a slight loss of colour. Two thicknesses of paper are taken because one alone is liable to break ; and the paper should be used dry, for, if previously wetted, the water will weaken the colour of the solution ; and it ought to be cut to a size not exceeding $4\frac{1}{2}$ inches to prevent undue absorption. If the metal to be examined contains more than 0.8 per cent. of carbon, 0.5 gramme, or less of it, may be taken, or the solution may be diluted with an equal volume or more of water and the proper allowance made ; or an instrument of higher range may be used. On the other hand, if the metal contains a very small percentage of carbon, 2 grammes of it may be taken. For preparing the standard solutions (the normal ones begin to lose colour after some hours), caramel dissolved in equal parts of water and alcohol, as suggested by Eggertz, answers well ; but with roasted coffee as the colouring matter the true shades may be obtained.

The following improvements on the process of Eggertz for determining combined carbon in steel has been devised by E. R. Taylor :—

A balance, consisting of a very fine thread of glass with a pan in two parts, one a cup and one a cone, serves to weigh the steel. A horizontal drill with a glass tube to form a hopper makes and conducts the drillings of steel as they are made to the balance-pan, which is properly supported about $\frac{1}{8}$ inch above a point to which it settles when

a 200-milligramme weight is placed in the pan. A sample of steel is placed in the drill-lathe, when the drillings, as before mentioned, fall into the pan below. As soon as 200 milligrammes have fallen into the pan the pointer sinks to the index and the drill is stopped.

By pressing a tube through a hole in the balance-table, the lip of the tube offering a support for the balance-cup, while the cone is pressed down with a pair of tweezers, the drillings at once fall into the tube and are ready for treatment with acid.

A glass funnel is made drawn out to a capillary orifice at the lower end. This is fused to a T-tube, the lateral branch of which is passed through the window of the laboratory to remove the fumes. A rubber nipple is fixed on the lower end of the T-tube into which the tube containing the steel is inserted; 8 c.c. are now drawn into the funnel tube and fall in drops upon the steel below. At the expiration of this action the tube is transferred to a bath kept at the temperature of 180°C . At the end of twenty minutes from drawing in the acid the operation is completed, the whole of the carbon has entered into a clear yellow solution which has a depth of colour proportionate to the amount of combined carbon in the steel. The tubes are cooled down to a normal temperature and compared with a series of standard colours, when it is easy to read off the amount of combined carbon in a sample of steel.

M. Sergius Kern gives the following notes on the copper chloride process for the determination of carbon in pig-iron and steel:—

1. In analysing pig-iron it is quite enough to take 0.2 to 0.8 gramme of the specimen; in analysing irons and steels 2 to 8 grammes. In preparing copper chloride, the solutions of copper sulphate and sodium chloride must be neutral and heated to 85° . For dissolving every 0.1 gramme of the specimen 20 c.c. of concentrated copper chloride solution is used.

2. The glass with specimen and copper chloride solution is left for two days at the ordinary temperature; every three or four hours the solution is carefully stirred with a glass rod. When no coarse particles remain on the bottom of the glass the solution is placed on a sand-bath and gently heated to 50° to 60° for about three hours. An excess of hydrochloric acid is next added, and the analysis is concluded in the ordinary way.

8. Pig-irons containing manganese in notable quantities are dissolved entirely in copper chloride in about 6 to 8 days; ferro-manganese requires not less than 10 days.

4. The filtration through asbestos filters must be always executed as quickly as possible; in this case Weil's apparatus is very handy. The construction of it is described in Dr. Fresenius' 'Quantitative Analysis' (sixth edition).

Mr. G. S. Packer proceeds as follows:—2.5 grammes of pig iron are treated with 50 to 60 c.c. of copper sulphate (1.5), and after standing 7 to 8 minutes in the cold the solution is gently warmed, until

the iron is completely dissolved ; there is then added 20 to 25 c.c. of copper chloride (1·2) and 50 c.c. of pure strong hydrochloric acid, and the solution is gradually brought to boiling ; by this time the precipitated copper should be redissolved (time, 45 to 50 minutes) ; it is then filtered through an asbestos filter, made as follows :—

The usual asbestos funnel—a tube about 8 inches long and 1 inch diameter, drawn out at one end to a neck about $\frac{3}{8}$ inch diameter—has some pieces of very thin glass rod, about $\frac{1}{2}$ inch long, placed side by side firmly in the narrow end, and above these some previously ignited asbestos loosely plugged, about $\frac{1}{2}$ inch thick ; some hot water is then run down the funnel to consolidate the asbestos, and the solution is then filtered and washed in the usual way.

This filtration and washing can be done in 5 to 7 minutes, unless the iron be very silicious, when it sometimes takes 20 to 30 minutes ; if the solution be allowed to boil for some time, or even stand (overnight, for instance), the silicium forms gelatinous silica which greatly hinders filtration. The asbestos and carbon are now placed in a 200-c.c. flask with 8 grammes oxalic acid, using as little water as possible for rinsing in ; the flask is fitted with a 2-ounce stopcock-funnel and delivery-tube to conduct the gas first through a U-tube containing some strong sulphuric acid only (a wash-bottle and sulphuric acid allows the acid to run back if a draught should blow the light under the flask a little on one side for an instant), and then through one containing broken glass and sulphuric acid, and then into potash bulbs. The funnel is filled with strong sulphuric acid (40 c.c.), and when the connections are all made, the acid is allowed to flow slowly in, the solution is gradually brought to boiling and kept so a minute or two, till all evolution of gas ceases ; air is then drawn through the apparatus, allowing it first to pass through potash solution to absorb atmospheric carbonic acid, and the bulbs weighed. Time $1\frac{1}{4}$ to $1\frac{1}{2}$ hour.

Estimation of Sulphur in Iron and Steel.

The plan usually adopted is to dissolve a weighed quantity (about 3 grammes) of the metal in strong nitric acid, adding a little hydrochloric acid occasionally, and evaporating the solution to dryness. Dissolve the residue in very dilute warm hydrochloric acid, and precipitate the sulphuric acid in the solution by means of barium chloride. If the precipitated barium sulphate, after washing once or twice by decantation, has a yellow or brown colour, owing to the presence of iron mechanically carried down, heat it, before filtering, with dilute hydrochloric acid.

Mr. H. B. Hamilton dispenses with the direct oxidation of the sulphur with nitric acid and evolves it as sulphuretted hydrogen, which is more easily oxidised. A weighed quantity of iron in a fine state of division (for puddle bars not less than 10 grammes) is thrown into a capacious flask, about an ounce of water is added, and the whole agitated to pre-

vent caking in the after process. A cork is inserted into the mouth with two perforations—the one for a safety funnel tube to admit acid, the other for a tube bent at right angles. The latter tube communicates with a U-tube containing a solution of caustic potash free from sulphate. Either concentrated hydrochloric acid or water is to be poured in at the funnel, according to circumstances. As soon as the action, after pouring enough hydrochloric acid into the flask, has almost ceased, the contents of the latter are to be boiled. The flame is then taken away, and, as soon as the ebullition has ceased, air is sucked through the apparatus for about a minute. This process may be repeated, if, as will easily be discovered, the action of the acid has not entirely ceased. The contents of the U-tube are emptied into a beaker, and the tube rinsed out with distilled water. A current of chlorine is allowed for some time to pass through the solution, which is then boiled, acidulated with hydrochloric acid, and boiled again, to drive off all hypochlorous acid, when it is precipitated with barium chloride. The contents of the flask are filtered through asbestos, and, without washing the residue at all, it is transferred again to the flask, removing every particle from the funnel by means of a small quantity of nitro-hydrochloric acid. After heating, in order to oxidise the black residue with the nitro-hydrochloric acid, water is to be added, and some sodium carbonate, free from sulphate, to neutralise the large excess of acid. After boiling, filter, taking care that the solution is still slightly acid; precipitate with barium chloride, add the solution with precipitate suspended in it to the former one, and proceed in the usual manner.

Dr. Eggertz, to whom analytical chemistry is indebted for the colorimetric process of estimating combined carbon in iron and steel, has devised an equally expeditious plan for estimating the sulphur. He takes one decigramme of cast-iron, wrought-iron, or steel, cut up or pulverised, and passed through a sieve with holes not larger than 0.6 millimetre, and introduces it, by means of a glass or glazed paper funnel, into a flask about 0.15 metre high and 5 centimetres diameter, previously containing 1 gramme of water and 0.5 gramme of concentrated sulphuric acid; or, in preference, 1.5 gramme of sulphuric acid, sp. gr. 1.25, and whose volume (1.5 c.c.) has been marked on the flask. A piece of polished silver plate (18 millimetres long, 7.5 millimetres wide, and 1 millimetre thick, with a hole at one end), composed of 75 per cent. of silver, 25 per cent. of copper, and attached to a thin platinum or silver wire, is quickly introduced into the flask, so that it may be a little below the neck; a cork is put in so as to hold the wire without completely closing it. It is allowed to stand 15 minutes at the ordinary temperature, and the silver plate is then removed. If the iron contains sulphur, the plate is coloured by the sulphuretted hydrogen gas disengaged during the solution of the iron in the dilute sulphuric acid; and, according to the amount of sulphur present, the colouration of the plate passes to a coppery yellow, a bronze brown, a

bluish brown, or a blue. These colourations are determined with the greatest accuracy—especially that of the silver plate alone, No. 1; that of coppery yellow, No. 2; that of bronze brown, No. 3; that of blue, No. 4. The intermediate degrees may be represented by decimals, thus: 2·5 if the colouration is between 2 and 3; 3·1 if the plate is one-tenth towards the blue; 8·5 if it is as much blue as brown; 8·9 if the brown colouration is feeble.

As the normal colouration No. 2, Dr. Eggertz has adopted that of the bronze called yellow metal, newly rubbed with fine sand on leather. (This metal consists of 60 parts of copper and 40 of tin.) For the colouration No. 3, a convenient alloy has not yet been found. A bronze, consisting of 85 parts of copper and 15 parts of zinc, does not quite represent the colour which should be obtained, for when freshly cleaned it is too bright, and at last takes a bluish colouration. For the colour in question it is better to use a plate of silver which remains in the flask during the solution of the iron, until it has become as brown as possible, and a slight bluish colour begins to be perceived; the plate is then removed and preserved in a well-closed tube. The colouration No. 4 resembles that of a watch-spring. If the amount of sulphur is very considerable, this colouration passes to a clear bluish grey. By passing the plate of silver over a bottle of ammonium sulphide the desired number can be easily obtained. To obtain in these assays for sulphur the proper tint on the silver plate, it is necessary to take certain precautions. The plate is to be held with pincers and cleaned as well as possible by rubbing it with a soft leather on which is placed a little very fine rotten-stone. Contact with the fingers is avoided by means of a piece of paper, and the plate is to be carefully dried with a piece of filtering paper. If the plate, by cleaning or by the action of the burnisher, has been purified on its surface, this should be carefully removed by again rubbing with the leather, for pure silver is less sensitive to the action of the gas than that of the given standard. Thus it has sometimes been found that the silver employed for coinage furnishes less homogeneous plates, of which those parts richest in copper assume more quickly the blue colouration. On this account, the plates should be compared between themselves, by introducing them at the end of a wire into a flask in which iron is dissolving containing from 0·05 to 0·08 per cent. of sulphur. On introducing the plate, care must be taken not to turn the side but the edge against the strongest current of gas, which would otherwise colour one face of the plate more strongly than the other. The plate should be rapidly introduced into the flask after the introduction of the iron, as then a very strong disengagement of sulphuretted hydrogen immediately takes place. After a first experiment the flask is to be filled with water several times, so as to get rid of the odour of sulphuretted hydrogen. If a steel mortar is employed to pulverise the iron, the whole of the piece selected should be reduced to a very fine powder. The mortar should

be well cleaned each time, taking care to remove the disc from the bottom. Changes in temperature between 15° and 25° C. seem to have no sensible influence on the colouration of the metal; if the temperature exceeds 40° the plate becomes moist and gives false indications. Some practice is required to judge of the colouration of the plate, but it may be easily acquired. Generally the best plan is to place the standard plates of tints 1, 2, 3, &c., on a sheet of white paper by the side of the plate under experiment, exposing them to a good light near a window (but not sunlight), and to examine them with a lens. The colourations between 2 and 4 are the most difficult to recognise; but with a little experience none will vary more than 0.1, so that, for instance, the colouration may be estimated between 8.5 and 8.6.

The following is somewhat an approximation between the different colourations upon the silver plate and the amount of sulphur in a great number of different samples of iron:—

Number of the Colouration.	Percentage of Sulphur.	Number of the Colouration.	Percentage of Sulphur.
1.0	0.00	3.3	0.07
1.2	0.01	3.5	0.08
2.0	0.02	3.6	0.09
2.5	0.03	3.7	0.10
3.0	0.04	3.8	0.12
3.1	0.05	3.9	0.15
3.2	0.06	4.0	0.20

It is evident that in this way the exact quantity of the sulphur is not determined; but several years' experience have shown that if these experiments are made with care, and the quantity of sulphur does not exceed 0.1 per cent., the results are near enough for all practical purposes. Iron which does not colour the silver plate will sometimes produce a colouration if we double the quantities of iron and acid. With half the quantities of acid and sulphurised iron, silver generally gives a little more than half the real quantity of the sulphur which is present.

Amongst experiments on the estimation of sulphur in iron, the following deserve mention:—1. The quantity of sulphur in wrought-iron is often so small that it produces no colouration on the silver plate; this iron, therefore, not being red-short, may be employed for all kinds of uses. It must not, however, be forgotten that the quantity of sulphur is not equally distributed throughout a piece of iron, but that it may vary considerably in different places. On experimenting with the turnings obtained from a portion of an iron bar which was visibly red-short, a stronger tint is often obtained on the silver plate than when using other parts of the bar. The fragments obtained from red-short iron in boring a horseshoe do not often give on the silver plate a deeper colouration than 2, and it appears to follow that ordinary wrought-iron which contains 0.02 per cent. of sulphur in certain parts cannot conveniently be employed for this purpose. If the red-short

iron gives to the plate a slighter and more feeble colouration than 2, it may be supposed that the breaking is due less to sulphur than to an insufficient working of the cast-iron, the crude pieces in wrought-iron entirely free from sulphur often acting as if they were red-short. In general it appears certain that the quantity of sulphur in iron is more injurious when the iron has been badly worked. In a hard iron melted in a steel crucible, we may, in spite of its containing 0.04 per cent. of sulphur, make holes like those in a horseshoe without any trace of cracks, which may undoubtedly be attributed to the homogeneousness and good working of this iron; the quantity of phosphorus being only 0.08 per cent. The lower portion of an English rolled rail, without fault, contained 0.11 per cent. of sulphur and 0.8 per cent. of phosphorus; a portion was cut off which was so red-short that it could not be made use of.

2. The amount of sulphur in steel of the best quality is such that the colourations on the silver plate vary only between 1 and 1.5. As in the case of wrought-iron, the quantity of sulphur often varies in different parts of the same piece of steel, and that also appears to be the case in a little less decided manner in cast-steel.

8. The quantity of sulphur in cast-iron is rarely so little as not to colour the plate. In the greater number of Swedish cast-irons, this quantity is such that the silver plate varies in colouration between 2 and 3. In iron for gun castings it is between 8.3 and 8.7, and sometimes more. In cast-iron the quantity of sulphur is often distributed unequally; there is generally more on the surface than is met with below. If the colouration of the silver plate does not exceed 3, we can assume that the cast-iron refined in the ordinary manner will not give red-short iron, especially if the refining is done carefully. But as in different methods of refining different quantities of sulphur may be removed from the iron, and, in general, more if the iron is the result of a light charge of the blast-furnace, it cannot be said beforehand that all cast-iron, which communicates a bluish colouration to the plate, will necessarily give red-short iron. This will be the case, however, with cast-iron which colours the plate as deep a blue as that of a watch-spring. In cast-iron, which gives a red-short wrought-iron, without rendering the silver plate more than brown, it is probable (the iron having been well refined) that the cause is owing to the presence of other substances than sulphur, but this occurrence is very rare. Many circumstances appear to show that the quantity of sulphur in iron diminishes with time, at least on the surface, and under favourable conditions.

The quantity of sulphur in a mineral cannot be estimated in the manner just described; all that can be done is to estimate the sulphur in the cast-iron, which is obtained by reducing the mineral in a crucible. Attention must always be paid to the following:—*a*. That the powdered charcoal which fills the crucible is free from sulphur. This is ascer-

tained by fusing iron, as free as possible from sulphur, in a crucible filled with the same powdered charcoal, and then examining the regulus obtained. If this latter gives a higher amount of sulphur than the iron originally contained, the cause is attributable to the charcoal. At Fahlun the charcoal absorbs, in a short time, much sulphur from the smoke of the burning pyrites; and the powder selected for the crucible experiments in the Mining School is obliged to be kept in closed vessels. If the charcoal employed as a combustible in the crucible furnace is exposed to the action of much sulphuretted hydrogen or sulphurous acid, the experiments show it. *b.* The state of the mineral, whether unroasted, badly roasted, or well roasted. The small laboratory experiments, having for their object to ascertain how much sulphur can be removed from a mineral by roasting in bulk, are always inexact. *c.* The influence exerted on the quantity of sulphur by the minerals mixed with it. It follows, from many experiments made at the Mining School, that the more silicic acid the slag contains the more sulphur the cast-iron receives, and that the quantity of sulphur gradually diminishes in proportion as the quantity of lime is increased. In general, assays for sulphur should be made with regulus obtained from a mixture containing as little lime as possible, but giving vitreous slags. If the colouration of the silver plate does not exceed No. 8, the quantity of sulphur may be considered as insignificant, especially in experimenting on non-roasted minerals.

The lime used in blast furnaces may be assayed for sulphur in the following manner:—Mix 0.8 gramme of rich and pure iron mineral with 0.2 gramme of quartz and 0.2 gramme of lime; fuse the mixture as usual in a crucible, and assay the resulting iron for sulphur. In this manner it may be ascertained if the lime contains an injurious dose of sulphur. If it were chemically pure we should obtain, by the addition of 2 or 8 per cent. of clay or talc, free from sulphuric acid, a better slag. If, on the contrary, the lime contains much silicic acid, more than 0.2 gramme should be taken for the experiment.

Estimation of Sulphur in Iron Ores.

Five grammes of the mineral, ground as finely as possible in an agate mortar, are treated with potassium chlorate and hydrochloric acid. After desiccation and extraction with hydrochloric acid and water, the insoluble substances may be lead, calcium, barium and strontium sulphates, silica, and undecomposed mineral. By stirring well and filtering the liquid whilst warm, the two former salts may generally, however, be dissolved. The filtration should be performed through a double filter, to prevent the pulverised mineral from passing through. When the clear portion of the solution has been poured upon the filter, add to the insoluble matter 5 c.c. of hydrochloric acid and 5 c.c. of water; then leave the mixture for two hours on the water-bath at a

boiling temperature, when, if care be taken to stir well, the calcium sulphate will be completely dissolved. Wash the insoluble portion in warm water, and pour it on a filter, taking care to place below a flask specially to receive that portion of mineral which may have passed through the filter. The filtered liquid, whose volume is about 50 c.c., should be rapidly boiled and mixed with 2 c.c. of a saturated solution of barium chloride. (This amount is sufficient to precipitate the sulphuric acid formed from 0.1 gramme of sulphur.) After cooling add to the mixture 5 c.c. of ammonia, sp. gr. 0.95, then stir well with a glass rod, and leave the whole to rest at the ordinary temperature for twenty-four hours. The clear solution should be decanted as completely as possible on to a strong filter, and the precipitate stirred up with about 20 c.c. of cold water, and then left to itself until it has quite settled. If warm water is used without having added a few drops of hydrochloric acid, a little iron oxide will precipitate. The clear liquid is likewise thrown on to the filter, and the operation is repeated several times with cold water, and then two or three times with boiling water, without which precaution the barium sulphate will pass through the filter. Finally collect the precipitate, and wash it with warm water. The last drops of this water, on being evaporated on a watch-glass, ought not to leave more than a scarcely visible white ring. The precipitate is then dried, heated to redness, and weighed. If it is coloured with iron oxide it must be washed with a little hydrochloric acid, dried in the water-bath, and taken up with a few drops of acid and water, and then the preceding operation repeated (washing, drying, igniting, and weighing). If the precipitate has only a feeble red colour, which is often the case, this latter operation will be unnecessary.

To dissolve the lead sulphate which may occur in the insoluble portion, remove this from the filter with the end of a feather, introduce it into a flask, and pour over it 10 c.c. of concentrated ammonium acetate. The solution, after having been strongly agitated and heated in the water-bath, is carefully poured on to a filter. Then wash the residue with a little ammonium acetate, and repeat the treatment until a few c.c. of solution, acidulated with a little acetic or hydrochloric acid, is not rendered turbid when warmed with barium chloride solution. The filtrate is then diluted, slightly acidified, and the sulphuric acid precipitated by means of barium chloride. After the lead sulphate has been removed, there may still occur barium and strontium sulphates in the insoluble portion. To decompose these salts the residues must be dried, heated to redness, and weighed, and then fused with five times their weight of pure dry soda. The mass is digested with water over a water-bath, the liquid filtered, and the residue washed with warm water. The silicic acid is separated from the solution, which contains the silicate, the carbonate, and the sodium sulphate, by adding hydrochloric acid and drying on the water-bath. After filtering, precipitate the solution with barium chloride. To ascertain if the iron

mineral contains gypsum or other soluble sulphates, take 5 grammes, place them in 20 c.c. of hydrochloric acid and 60 c.c. of distilled water, and digest them for three hours on the water-bath, with frequent agitation. The filtered solution is mixed with barium chloride and 15 c.c. of ammonia; then proceed as already described. If there are present in the mineral grains of iron or copper pyrites, or galena, they will only give traces of sulphuric acid in this operation.

To ascertain the accuracy of the process which has just been described, the following experiments were made by Dr. Eggertz:—

Experiment I.—Iron sulphide (as usually employed in the preparation of sulphuretted hydrogen) was dissolved, as above described, in hydrochloric acid, water, and potassium chlorate, in a flask furnished with a glass tube leading into a solution of copper sulphate. No trace of precipitate, nor any colouration which would indicate the presence of copper sulphide, could be detected in the solution; so that it is certain that no loss of sulphur could take place on dissolving iron or minerals in this manner. When the experiment was repeated, but with this modification, that the solution of potassium chlorate, during the addition of hydrochloric acid, was not kept well boiling, the copper sulphate solution was rendered turbid, showing the necessity of resorting to complete ebullition.

Experiment II.—Iron sulphide treated in the same apparatus with aqua regia (composed of equal parts of nitric and hydrochloric acids) requires a more equal temperature and a stronger ebullition to prevent any precipitation of copper. Moreover, as the solution of iron by potassium chlorate takes place promptly, and as the presence of nitric acid is prejudicial both for the solution of the mass after drying in the water-bath (owing to the formation of iron subnitrate), and also for the precipitation of the solution by barium chloride, preference should be given to the employment of potassium chlorate.

Experiment III.—One gramme of pure pyrites was treated in the manner above described, and the sulphur which separated at first was completely dissolved during the drying of the liquid on the water-bath. Upon precipitating with barium chloride a quantity of barium sulphate was obtained, exactly corresponding to the amount of sulphur in the pyrites.

Experiment IV.—Many experiments were made with the filtered liquids obtained from solutions of iron which had been freed from sulphur by excess of barium chloride. After standing for several days these were brought to ebullition and mixed with 1 c.c. of an aqueous solution of sodium sulphate, containing a quantity of sulphuric acid corresponding to 0.0001 gramme of sulphur. At the end of at least 24 hours a feeble precipitate is observed, which proves that the sulphuric acid is perfectly separated from the iron. This precipitate is rendered distinctly visible when the contents of the flask are stirred by moving a glass rod circularly round the liquid, for the barium sulphate

then mounts in a small whirlpool and falls again on to one spot. When, also, 50 c.c. of the solution of sodium sulphate are added to the filtered liquids, the corresponding weight of barium sulphate has been obtained. If, in the filtered liquids, there were 10 c.c. of free hydrochloric acid instead of 5, two days sometimes elapse before the precipitate from the solution (containing 1 c.c. of the sodium sulphate solution) becomes visible. Consequently, if there are more than 5 c.c. of free hydrochloric acid in the solution, there must be added for each c.c. in excess (to the solution after addition of barium chloride and then cooling) 1 c.c. of caustic ammonia, so as to nearly neutralise the hydrochloric acid.

Experiment V.—In many experiments in which the barium sulphate was washed for a long time on a filter, both with warm and cold water, it was impossible, upon evaporating a drop of the filtrate on a watch-glass, to avoid traces being left on the latter. Some drops of a solution of barium chloride and a little hydrochloric acid added to the filtrate always produced a feeble white precipitate by the action of heat. For this reason the washing should only be continued until a drop of the washing water leaves, on evaporation on glass, an *almost* imperceptible white ring.

Experiment VI.—4.9 grammes of calcium carbonate and 0.1 gramme of pyrites submitted to the same process of solution gave, by evaporation on the water-bath, a perfectly clear liquid; after drying, 6 c.c. of hydrochloric acid and 50 c.c. of water were added to the residue, and there was thus obtained a considerable mass of gypsum. On leaving the liquid for an hour on the water-bath and increasing the quantity of water, the gypsum was completely dissolved.

One decigramme of gypsum was dissolved in 2 c.c. of hydrochloric acid and 4 or 6 c.c. of water (or, better still, in 10 c.c. of ammonium acetate). The solution was kept for half an hour on the water-bath with frequent agitation. It could then be diluted with water at pleasure, without the gypsum being precipitated.

Experiment VII.—0.5 gramme of galena was completely dissolved in the same manner, and the solution brought to dryness on the water-bath. A little water was added to remove the potassium chloride, and evaporated after solution of this salt; the lead sulphate which remained was then completely dissolved in 20 c.c. of ammonium acetate, and precipitated with barium acetate containing a little free acetic acid. The barium sulphate, which was of the proper weight, was of a grey colour, but became whiter without alteration of weight by being heated to bright redness for some time with access of air.

One decigramme of lead sulphate dissolves without rise of temperature in 2 c.c. of ammonium acetate; lead chloride dissolves in it still more easily. The solution may be diluted with water without any precipitation taking place.

One decigramme of lead sulphate was dissolved on the water-bath

by violent agitation for half an hour with 4 c.c. of hydrochloric acid (of 1·12 sp. gr.) diluted with 2 c.c. of water; but the sulphate commenced to crystallise as soon as the liquid was cooled to 60° or 70°.

Experiment VIII.—4·7 grammes of an iron mixture containing a known quantity of sulphur having been mixed with 0·1 gramme of pyrites, 0·1 gramme of lead sulphide, and 0·1 gramme of gypsum, treated in the same manner as the iron mineral, gave exactly the quantity of barium sulphate which it should have yielded by theory. The precipitate from the solution in ammonium acetate only weighed a few milligrammes.

Experiment IX.—An aqueous solution of sodium sulphate, accurately standardised, and then barium chloride, were added to a solution of soluble glass acidulated with hydrochloric acid. The weight of the barium sulphate which was formed showed that the gelatinous silicic acid dissolved in the acid does not interfere in these experiments.

Experiment X.—0·1 gramme of pure quartz was fused with 0·5 gramme of anhydrous soda in a platinum crucible. The mass was completely soluble, without heating, in 5 c.c. of water, and the liquid remained clear even in the water-bath.

Experiment XI.—0·1 gramme of barium sulphate was fused in a platinum crucible with 0·5 gramme of sodium carbonate, the mass, treated with water, was poured upon a filter and washed. The barium carbonate remaining on the filter was brought to a red heat, and then dissolved in dilute hydrochloric acid without the least residue. The same experiment was tried with strontium sulphate. It follows, therefore, that these two salts may be completely decomposed by fusion with sodium carbonate.

Estimation of Silicon in Iron and Steel.

All who are occupied in the analysis of iron and steel are aware how very uncertain the determination of silicon is when the method hitherto used for its separation is followed, because cast-iron, and even bar iron and steel, are never found absolutely free from intermingled slag. This slag is decomposed by the ordinary method of dissolving the iron in acids, and its silica then augments the amount of silica formed from the silicon contained in the iron or steel. This cannot be said of every sort of cast-iron, but these sometimes contain blast-furnace slag, although pig-iron containing slag may be considered as rare. It ought also to be mentioned that crystallised silicon has been found in crystallised cast-iron from Carinthia, in the form of small silvery plates, which were neither acted upon by boiling aqua regia nor by ignition in oxygen gas; but they were converted into silica by fusing with potassium and sodium carbonates.

Crystallised silicon is insoluble in hot solutions of sodium carbonate, but is soluble, with development of hydrogen, in hot solutions of caustic potash, and also in hot hydrofluoric acid. The accurate estimation

of the silicon in iron and steel has been effected by Dr. Eggertz, who, after fruitless efforts to dissolve iron in highly diluted organic or inorganic acids, which should have no effect on the refinery slag, finally discovered such a solvent in bromine, which, when mixed with water, dissolves the iron without the slightest action on the accompanying slag. But as working with bromine in large quantities is very disagreeable, trials were made to use iodine instead; and this, like bromine, has been proved to have no effect on the slag, nor on the iron oxide or proto-sesquioxide, or manganese proto-sesquioxide. At the same time, bromine dissolves iron quicker than iodine, and is, perhaps, more easily obtainable in the requisite state of purity. Moreover, as continued experiments have shown that a solution of sodium carbonate can separate finery slag from the silica which has been formed by the use of iodine or bromine on the silicon contained in the iron, the following method for the determination of silicon and slag in bar iron or steel has been used and considered successful; the same method may be employed for cast-iron, because blast-furnace slag, when such is found, is not perceptibly changed by iodine or bromine, nor by solutions of sodium carbonate. Three grammes of bar iron or steel which have passed through a sieve of 0.2 of a line are taken for analysis. Fifteen grammes of iodine are added in small portions at a time to 15 c.c. of water in a beaker of 100 c.c. capacity. The water must be previously boiled to expel the air, which would otherwise oxidise the iron. The iodine is stirred in the water with a glass rod, in order to get rid of the air which has accompanied it, and the floating iodine particles are allowed to sink. The beaker with the iodine and water, which is kept covered with a watch-glass, is cooled in ice before the iron is put in, and during the solution it is kept at the temperature of 0° C. For the first few hours it must be well stirred every hour, or oftener, with a glass rod, but afterwards not so frequently. In consequence of the low temperature and the careful admixture of the iron (by which heat is prevented), the solution may be performed without the least development of gas, and the iron has less tendency to become oxidised by the air when at this low temperature. By pressure, and by agitating with the glass rod, the solution of the iron particles which collect at the bottom of the beaker is much facilitated; if no lumps of iron particles are visible, the beaker may be kept at the ordinary temperature, or, preferably, in ice water. If some of the solution has dried on the sides of the beaker or on the glass rod, it must be well moistened with the same solution before water is added. About 80 c.c. of water, which should be very cold in order to prevent the formation of basic salts, are added to the solution; it is then well stirred, left to settle, and the fluid with the lighter particles of graphite is poured on to a filter of 2 inches diameter; the filtration is kept up without interruption until there remains only a somewhat heavy dark powder of slag, &c., at the bottom of the beaker; about 5 c.c. of water,

with a few drops of hydrochloric acid, are now poured in and stirred with the glass rod; if hydrogen is given off, it is an indication that there is still some metallic iron undissolved. The acidified water is quickly poured on the filter, in order not to act on the slag. If a development of gas is perceived, a little iodine, with sodium carbonate and water, is added for the complete solution of the iron, and the residue is thrown on the filter and washed with cold water, until a drop of the filtrate gives no reaction with a solution of 0.2 per cent. of potassium ferrocyanide contained in a small porcelain crucible. Solutions containing 0.00001 gramme of iron oxide per c.c. show in this way very distinct reactions, particularly if a drop of dilute nitric or hydrochloric acid be added. The filtrate is evaporated to dryness, in which operation some of the iodine is sublimed away. Thirty c.c. of hydrochloric acid, 1.12 sp. gr., are then added, and it is again evaporated in order to obtain the silica which may be dissolved in it. The filter, previously dried and weighed, is again dried and weighed when containing the precipitate. It is then ignited, and the residue weighed. After ignition, the residue is boiled in a solution of soda, in order to extract the silica, and weighed. It should be observed that some part of the silica which has been formed from the silicon in the iron may possibly unite with the slag during the drying and ignition. In consequence of this, it is difficult to extract it by means of a soda solution, whence this method is not to be recommended in exact determinations of silicon.

When using bromine as a solvent, 6 c.c. must be taken to 8 grammes of finely-powdered iron or steel, with 60 c.c. of water, which has been previously boiled, and cooled to 0° C.; and this temperature must be preserved by placing the beaker in ice water until the solution is complete, which usually takes place in two or three hours; it is cautiously stirred once or twice with a glass rod; if stirred hastily, the solution proceeds too violently. The further operations are conducted in the same manner as when using iodine. The bromine is most conveniently preserved under water, and is taken up by a pipette, which is introduced into the bottle, the upper end being closed by the finger.

When it is preferred to dissolve iron or steel in lumps instead of in powder, this may be done; but it is not then necessary to place the beaker in ice water, as the metal is less violently acted upon in this form. Several days are required for the solution; the iron, and particularly the steel pieces, must be occasionally cleaned from the graphite which adheres to their surface.

In order to determine the silica (formed from the silicon in the iron) and slag, the filter, which contains graphite (in combination with iodine or bromine and water), silica, and slag, is unfolded, whilst it is still wet, on a watch-glass. The contents are washed away from the filter (these should only occupy the lower half of the filter whilst in

the funnel) with a very fine jet from a wash-bottle (so as not to obtain too much water) into a platinum or silver crucible of the capacity of 80 c.c. The loosening of the mass may be facilitated by a fine camel-hair pencil. The water in the crucible is evaporated to about 6 c.c., then mixed with 8 c.c. of a saturated solution of sodium carbonate, free from silica, and the crucible put in a water-bath. It is kept in the boiling water one hour, during which time the liquid is stirred two or three times, and the insoluble mass crushed with a platinum spatula. The supernatant liquid is carefully poured from the insoluble mass on to a small filter, and to the mass in the crucible are added 1 c.c. of saturated solution of sodium carbonate and 2 c.c. of water. When this has been boiled one hour, the whole contents of the crucible are thrown on the filter and washed. The solution of silica in soda is acidified by hydrochloric acid, and mixed with the iron solution, and the whole evaporated to dryness on a water-bath. When the solution attains the thickness of ordinary syrup, it is stirred very often with the glass rod, until the mass becomes a dry powder, and heated until the smell of hydrochloric acid has nearly gone off; the beaker is then placed in boiling water for 6 hours, 15 c.c. of hydrochloric acid of 1.12 sp. gr. are then added, and the beaker left on the water-bath one hour. As soon as the red powder is entirely dissolved, 50 c.c. of water are added; and when no crystals of iron chloride are visible, the solution is thrown on a filter and washed with cold water, warm water forming basic iron salts which make the silica appear red. The filter containing the silica is dried and ignited in a porcelain crucible, gradually increasing the temperature to a full red heat, and weighed; if the silica is coloured red by iron oxide, a little hydrochloric acid, 1.19 sp. gr., must be poured into the crucible. One decigramme of ignited and pure silica obtained from analysis will dissolve in the above manner in 6 c.c. of a saturated soda solution and 12 c.c. of water. If any residue is observed after the second boiling, this arises from some impurity which has united in small quantities with the silica, rendering it insoluble. When strong hydrochloric acid is boiled with this insoluble silica, it may afterwards be dissolved. When the solution of silica is diluted with water to the volume of 50 c.c. at the ordinary temperature, it has no tendency to come into the form of jelly. Quartz powder is dissolved by the preceding method, but very slightly; but ignited titanitic acid and finery slag are not acted upon, and the tersilicate slag from blast-furnaces but very little.

When the silica is quickly exposed to a high temperature, a considerable loss may arise from the spiriting of the water combined with the silica. Silica dried at 100° C. has been proved to retain 1 equivalent of water to 3 equivalents of silica—that is, about 6 per cent. of water, which is lost by a strong ignition. The iron oxide is easily dissolved in the heat of a water-bath. The silica is again thrown on a filter, washed, dried, ignited, and weighed.

To ascertain the purity of the silica, it may be mixed in a platinum crucible with ten times its weight of pure ammonium fluoride, diluted with water to the thickness of syrup. The water must be evaporated on a water-bath, and the crucible heated, with a cover on it, by a gradually increasing heat over a spirit-lamp to a full red. If nothing is left in the crucible, the silica was pure, and has passed off as silicon fluoride; but, if anything remains, the operation with ammonium fluoride must be repeated until a constant weight is obtained. When iron contains tungsten, some tungstic acid is formed, and this accompanies the silica for the most part, being dissolved by the soda solution, but it is not volatilised by the use of ammonium fluoride. Vanadic acid also accompanies the silica, behaving as tungstic acid. Instead of using ammonium fluoride, it is preferable to use hydrofluoric acid, with which the silica is moistened, and the evaporation is conducted on a water-bath. The mass left on the filter from the soda solution may be composed—besides graphite—of slag, iron oxide, titanium oxide, &c. (but not copper, at least when the iron does not contain more than 1 per cent.); this is dried, ignited, and weighed. The method of separating iron oxide and slag, when the iron or steel contains both these, is not yet known. If the composition of slag were always alike (which it is not) it would be easy to calculate its amount from either the silica or iron oxide obtained in the analysis. In a piece of very red-short Bessemer iron which contained no sulphur, by several experiments 0·8 per cent. of iron oxide has been obtained, and only traces of silicon. After ignition, the iron oxide may possibly be found as sesquioxide. The amount of oxygen, in case the red-shortness is due to this, as it probably is, amounts to less than 0·1 per cent.

When the iron or steel for analysis contains titanium, a part of this substance follows the slag in the form of titanitic acid. If such is the case, this must be melted with ten times its weight of acid potassium sulphate, by which it is dissolved; the mass is dissolved in cold water, and the solution precipitated by boiling; the weight is determined, and subtracted from that of the slag. (See Titanium, pp. 98, 94, and chapter on Silicates.)

In respect to the determination of silicon in cast-steel where only a trace of slag is found, the method given below for cast-iron may be employed; but 3 grammes at least ought to be taken for each experiment, and the acids for solution in proportion. The amount of silicon in bar iron and steel generally varies between 0·01 per cent. and 0·1 per cent.; but in two sorts of good cast-steel from Krupp's it has amounted to about 0·8 per cent. Slag in cast-steel has been found only in traces, but in another case it amounted to 0·2 per cent.; in good iron wire, prepared from bar iron, converted in a refinery hearth, from charcoal pig-iron, 0·33 per cent.; in puddled iron (armour plate), from 0·75 to 3 per cent.; and in an English iron rail, to 4 or 5 per cent.

For the estimation of silicon in cast-iron, in which no finery

slag is found, and only exceptionally blast-furnace slag, the following method has proved suitable:—2 grammes of iron, which has passed a sieve with holes of a diameter of $\frac{1}{16}$ inch at the most, is put into a beaker of 100 c.c. capacity, containing 80 c.c. of hydrochloric acid, sp. gr. 1.12. The beaker is covered with a close-fitting watch-glass, heated without delay, and the liquid kept in gentle ebullition for half an hour. All the carbon chemically combined with the iron is separated from the liquid in the form of an ill-smelling volatile hydrocarbon. If the carbon separated on solution is left in contact with the air some minutes before ebullition, it undergoes such a change that it does not go off in a volatile form; if necessary, some hydrochloric acid is added, and the solution evaporated to dryness on a water-bath. When the silica is red, strong hydrochloric acid is added, as previously described. If the silica is contaminated with titanitic acid, vanadic acid, or tungstic acid, it is operated upon with ammonium fluoride or hydrofluoric acid, as previously mentioned, whereby the silica is volatilised and calculated by loss. By the above method of dissolving iron in hydrochloric acid, the silicon changes, without evaporation, for the most part, to insoluble silica, which may be filtered and determined. Sometimes a very unimportant part is dissolved, especially if the boiling has been insufficient. When iron is dissolved in hydrochloric acid without heating (white cast-iron is very difficult to dissolve in this way), a still less portion of silicon is dissolved, and generally so little that it may be neglected for practical purposes. The washing is performed with hot water containing nitric acid as previously described. When the iron is dissolved in nitric acid, a great deal of silica enters into solution. The different sorts of cast-iron appear to be slightly different in this respect. In dissolving cast-iron by the aid of heat, in very dilute sulphuric acid, a great deal of silica is dissolved, but very little when the acid is strong; as the water evaporates, the silica separates and becomes insoluble.

The method given below rests upon these circumstances, and has proved very satisfactory, whilst the removal of the acid is avoided, which is both necessary and troublesome when using hydrochloric acid with heat. The amount of silicon has, according to both methods, turned out alike. Two grammes of cast-iron, which have passed a sieve of 0.2 of a line, are shaken by small portions at a time into a beaker of 100 c.c. capacity, previously containing 18 c.c. of water with 8 c.c. pure sulphuric acid of 1.83 sp. gr., with 6 c.c. of water. The beaker is covered with a watch-glass, and placed on a water-bath; if the graphite rises on the sides of the beaker, it is pushed down into the liquid by a glass rod. When the iron is dissolved, the watch-glass after being washed is changed for a paper cover, and the solution evaporated on a water-bath until no condensation occurs on a watch-glass held over the beaker; 80 c.c. of water are then added, and it is frequently stirred with a glass rod, whilst on the water-bath, until the

white iron salt has completely dissolved. The insoluble mass is then thrown on a filter, and washed with hot water containing 5 per cent. nitric acid, 1.2 sp. gr. (in order to dissolve all compounds of iron), as long as an iron reaction is given with potassium ferrocyanide. The filter, with its contents, is placed in a carefully tared porcelain crucible; it is then cautiously dried, ignited, and weighed. The purity of the silica is examined by the method previously mentioned, when considered necessary. If the cast-iron contains vanadium, this is obtained for the most part as a yellow-brown vanadic acid with the silica, from which it may be extracted by warm hydrochloric acid or by ammonia.

Mr. T. M. Brown proceeds as follows:—One gramme iron or steel is placed in a porcelain crucible with 25 c.c. nitric acid of 1.2 sp. gr. When the reaction is over, 25 to 30 c.c. dilute sulphuric acid—1 part acid and 8 water—are added, and the solution is heated till the nitric acid is entirely or nearly expelled. When the residue is sufficiently cool, water is cautiously added, and the contents of the capsule are heated till the crystals are perfectly dissolved. The solution is then filtered as hot as possible, and the residue washed first with hot water, then with 25 to 30 c.c. hydrochloric acid of sp. gr. 1.20, and finally again with hot water. After drying and igniting the silica is obtained snow-white and granular.

Mr. F. Watts gives the following process for the estimation of carbon and silicon:—The total carbon is first estimated by Wöhler's method, with the precautions to be described hereafter. Another weighed portion of the iron is similarly treated in a stream of chlorine, whereby not only the iron but the silicon, and probably the sulphur and phosphorus, are volatilised in the form of chlorides; the gas, as it issues from the combustion-tube, is caused to bubble through water contained in a flask, the water in the flask immediately decomposes the silicon tetrachloride, which is carried forward with the excess of chlorine, and soluble silica results. The water is afterwards evaporated to dryness, and the silica recovered and weighed. Unfortunately the presence of manganese is the source of a little difficulty, for its chloride is not sufficiently volatile to be readily removed from the contents of the boat by the stream of chloride. Hence, when manganese is present, which is almost always the case, it is necessary to wash the residue in the boat before weighing. The residue, which consists of the total carbon and the slag, having been weighed, from it is deducted the weight of total carbon previously estimated, the difference being the amount of slag. Thus, in two simple and rapid operations are estimated, first the total carbon, second the silicon and slag.

Regarding the process more in detail, the following arrangements are recommended:—It being necessary to obtain an efficient supply of chlorine which shall be well under control, some modification of the usual apparatus for generating the gas becomes desirable. A Woulff's bottle is filled with manganese ore in lumps; the necks are fitted with

two tubes, one of which passes to the bottom of the bottle, the other passes just through the cork, and is provided with a glass stop-cock. The bottle is placed in a saucepan of water, arranged so that it can be heated. The longer tube is connected with a stoneware jar containing common strong hydrochloric acid, this jar standing on a higher level than the generator; a gentle heat being applied to the saucepan, a supply of chlorine is obtained, which may be regulated at will. The stoppers should be of indiarubber well coated over with paraffin.

The chlorine before entering the combustion-tube must be rendered perfectly free from air and moisture. To effect this the gas is passed through three wash-bottles, the first containing water, the others strong sulphuric acid. The oxygen is removed by passing the gas through a tube containing lamp-black, which has been strongly heated in a crucible for half an hour to free it from moisture and tarry matter as well as to render it more coherent; the column of lamp-black is kept in position by plugs of gas carbon and should be about 6 or 8 inches long, occupying only the central portion of the tube. In practice it was found that the chlorine always contained moisture after passing through this carbon tube, and to this cause the discrepancies in the amounts of silicon found in the earlier analyses were probably due, for it is of the highest importance that the combustion-tube should be quite dry. Much better results were obtained when a tube containing pumice moistened with strong sulphuric acid was introduced between the carbon-tube and the combustion-tube.

The only part of the apparatus remaining to be described is the combustion-tube. This is a piece of ordinary combustion-tube, a portion of which, some 5 or 6 inches, is bent downwards at an angle of about 110° , so as to conveniently dip into a flask about a third filled with water. The carbon-tube, together with the drying and combustion-tubes, must be arranged to lie within the gutter of the combustion-furnace, the bent portion of the combustion-tube turned downwards and dipping into the flask placed at the end.

The method of procedure is as follows:—About 0.6 or 0.8 gramme of cast-iron, or about three times that quantity of wrought-iron or steel, in the form of borings, small lumps, or wire, is weighed in a porcelain boat; this is then introduced into a straight combustion-tube, taking care that the carbon in the carbon-tube is heated fully to redness, and the air in the apparatus and combustion-tube quite displaced by chlorine before the boat is heated. A slow stream of chlorine is steadily maintained and the boat heated gently, just sufficient heat being applied to volatilise the ferric chloride as it is formed. The stream of chlorine must not be too rapid or there is a danger of particles of carbon being carried out of the boat. When the whole of the iron is removed the boat is taken out whilst still warm, allowed to cool, thus becoming freed from any traces of chlorine, and the carbon estimated by combustion, in a separate tube, in oxygen in the usual way.

A similar quantity of the iron is weighed in another boat and the *bent* combustion-tube placed in the furnace, care being taken to free it entirely from any moisture. A flask of about 500 c.c. capacity containing about 100 or 150 c.c. of distilled water is arranged so that the extremity of the combustion-tube dips under the water; the air is carefully removed from the apparatus by passing a stream of chlorine, and the carbon-tube strongly heated. The boat is now introduced and the chlorine allowed to flow for a few minutes before heating; a gentle heat is now applied as in the previous instance, a higher temperature being induced towards the end of the operation.

When the whole of the iron is volatilised, a point most readily ascertained by the disappearance of red vapour, the tube is allowed to cool, the stream of chlorine being maintained for a short time, and the boat and flask removed. On removing the boats, they should in every case be placed at once in weighing-tubes, to preserve them from accident. The water is boiled, whilst still in the flask, until free from chlorine, and then evaporated to complete dryness in a platinum dish in the water-bath, the residue treated with a few drops of hydrochloric acid, well washed with warm water upon a filter, and ignited and weighed. This, less the filter-ash, gives the weight of silica, from which the percentage of silicon can at once be calculated. Should any silica adhere to the extremity of the combustion-tube, it may be detached by a glass rod, the extremity of which is covered by a short length of indiarubber tubing, a few drops of solution of caustic potash being employed if necessary.

A filter is dried at 110° , enclosed in weighing-tubes, and its weight ascertained; the contents of the boat are now emptied into this, well washed with hot water, and again dried at 110° and weighed. This is the weight of the mixed total carbon and slag, the percentage of which may be calculated. From this the percentage of total carbon already estimated is deducted, and the remainder reckoned as slag. The proportion of the slag can be checked by burning off the carbon from this mixture and weighing the residue. The object of washing the carbon and slag is to remove the less volatile chlorides. Earlier experiments, in which the washing of the residue was omitted, were far from satisfactory, for it was found impossible to entirely volatilise the manganese chloride, which, when the boat and its contents were ignited in oxygen, formed black glittering crystals of oxide upon its sides. This method enables the analyst to distinguish absolutely between the elemental and the oxidised portions of the silicon, and is specially distinguished for the short amount of time occupied. The removal of the iron from the sample by chlorine is accomplished in about a quarter of an hour, and the combustion of the residue can be proceeded with immediately, as it is not necessary nor desirable to allow the combustion-tubes to cool down completely between the successive operations.

The only obvious source of error was at the outset inquired into and found not to exist. It was thought possible that on treating in chlorine gas such a mixture of silica and graphite as cast-iron contains, a reaction would ensue, leading to the evolution of carbonic oxide and silicon chloride. But a blank experiment upon a mixture of finely-powdered blast-furnace slag and crystalline graphite showed that the mixture sustained no loss of weight by heating in chlorine gas, and no silica was found in the receiver.

The amount of silicon in grey charcoal pig-iron is about 2·7 per cent., and in spiegeleisen 0·8 per cent. The amount of silicon in pig from coke blast-furnaces is rarely more than 4 per cent. The least quantity of silicon in grey cast-iron is about 0·2 per cent., and in white (spiegeleisen) 0·01 per cent. The amount is usually from 1 to 2 per cent. in cast-iron suitable for the Bessemer process, and in pig-iron for puddling about 0·5 per cent. The amount of silicon in iron of different degrees of hardness from the same charge of the blast-furnace ought to be pretty well judged by the fracture, after some estimations have been made by analysis.

Estimation of Phosphorus in Iron and Steel.

The importance of ascertaining the quantity of phosphorus in iron is very great; for, although the presence of a very small trace of phosphorus in cast-iron does not produce any sensible modification in its properties, it nevertheless loses its most essential qualities when the proportion of metalloid amounts to some thousandths. Almost all the methods hitherto proposed consist in treating cast-iron with oxidising agents in such a manner as to cause the phosphorus to pass into the condition of phosphoric acid, which is estimated as a magnesian compound. M. V. Tantin, who has investigated this subject, states that several sources of error are inherent in this method, for the following reasons:—

1st. Part of the phosphorus escapes the action of the oxidising agents, and is evolved as a hydrogen compound.

2nd. It is necessary to work upon very dilute liquids, in order to avoid an admixture of iron oxide with the ammonio-magnesian phosphate; under these conditions it is difficult to collect the small quantity of phosphate disseminated upon the sides of the vessel in which the precipitation takes place.

3rd. Any arsenic which may be contained in the cast-iron will be contained in the precipitate as an arseniate, whose insolubility is equal to that of the phosphate.

In order, therefore, to avoid these sources of error, M. Tantin concludes that the best way of so doing will be to use a precisely contrary method, namely, by liberating the phosphorus as a hydrogen compound; but one objection naturally arises—will the whole of the phosphorus pass into the state of a gaseous product? Experiment

shows that there is not the least trace of phosphorus in the residue after the complete attack of the cast-iron by hydrochloric acid, which fact is not surprising if it be considered what strong affinity phosphorus has for hydrogen. The hydrogen phosphide produced by the action of hydrochloric acid upon cast-iron is almost always accompanied by sulphuretted, arseniuretted, and carburetted hydrogen. In order to effect the separation of these gases, first pass them into a Woulff's flask containing a solution of potash, which absorbs the sulphuretted hydrogen; the other gases are then made to pass through a solution of silver nitrate, which transforms the arseniuretted hydrogen into silver arsenite, soluble in the slightly acid liquid, whilst the phosphuretted hydrogen precipitates the silver and forms an insoluble phosphide. The phosphorus being thus completely separated from the sulphur and arsenic, its estimation is effected in a simple manner. The silver phosphide is treated with aqua regia, and thus transformed into silver chloride, and phosphoric acid which is precipitated in the state of ammonio-magnesian phosphate. To get accurate results by this process, the following precautions are indispensable:—

1st. The cast-iron must be attacked very slowly, or part of the phosphuretted hydrogen may pass through the solution of silver nitrate without being absorbed.

2nd. When the solution of the cast-iron is finished, a current of hydrogen, previously washed in lead acetate, must be passed through the flask.

Mr. Toash estimates the phosphorus in the following way. Three grammes of the iron are dissolved in aqua regia, the solution evaporated to dryness, and the insoluble matter filtered off. The iron perchloride solution is reduced to the state of protochloride, by heating with sodium sulphite. Although perfectly reduced, the solution still retains a yellow colour, due to dissolved organic matter. All excess of sulphurous acid is boiled off, a little iron perchloride is added, and the solution cautiously neutralised by means of sodium or ammonium carbonate, till the precipitate formed does not dissolve again. This small portion of iron peroxide precipitated contains all the phosphoric acid. It is filtered off, washed, redissolved in a little hydrochloric acid, mixed with some citric acid, and the phosphoric acid precipitated as magnesium ammonio-phosphate, the iron being held in solution in the ammoniacal liquid by citric acid.

Many skilful analysts consider that this method of throwing down the phosphorus as iron-salt and then estimating the phosphoric acid with magnesia, is unreliable, and prefer to employ the phosphomolybdate process. Other chemists, however, consider that the old plan is the preferable one. Dr. Noad says the following precautions are needed to ensure accuracy when dealing with iron and steel containing very small amounts of phosphorus. The solutions should not be too bulky. When estimating phosphorus in iron and steel,

from 75 to 100 grains should be taken, and the solution, at the time of adding the tartaric (or citric) acid, ammonia, and magnesium sulphate, must never be allowed to exceed in volume 8 fluid ounces. The first precipitate always carries down a little iron, which is removed by re-solution and re-precipitation after the addition of a fresh small quantity of tartaric acid. The first precipitate must not be collected till after the liquid has stood for twenty-four hours; the second precipitate is quite white, and may be filtered off after half an hour; it contains the whole of the phosphoric acid.

For estimating phosphorus in iron and steel, E. Agthe dissolves from 0.5 to 1 gramme of the specimen, according to the quantity of phosphorus supposed to be present, in 50 c.c. nitric acid; the solution is evaporated to dryness, the residue strongly heated, and afterwards—in order to expel the last trace of nitric acid—it is evaporated down again with hydrochloric acid. It is then redissolved in hydrochloric acid; so much hot water is added that the silica may separate out; the solution is filtered into a porcelain capsule, and evaporated on the sand-bath at a high temperature as long as everything dissolves on shaking the capsule. It is then further evaporated as far as possible at a lower temperature; but no firm, solid crusts must be formed. This evaporation must be conducted with especial care; if a little too much hydrochloric acid remains unevaporated the result will be too low, but if hard crusts are formed a clear solution cannot be obtained with nitric acid.

When cold, 85 c.c. of ammonia sp. gr. 0.96 are added and stirred up with a glass rod, so that a thick paste is formed. 75 c.c. nitric acid of 1.2 sp. gr. are then added; the capsule is set in a warm place and stirred to promote solution. The solution is rinsed into a beaker, and when no longer too hot, from 50 to 100 c.c. molybdic acid added, and well stirred; the beaker is set in a warm place (not above 80°) for four hours, let cool, filtered, and washed with dilute molybdic solution. The washed precipitate is dissolved upon the filter in a minimum of ammonia, and the ammoniacal solution is mixed with hydrochloric acid till the precipitate formed redissolves with difficulty. When the beaker is quite cold, 15 to 25 c.c. magnesia mixture are added; the whole is well stirred, filtered after standing for six hours, slightly washed with ammoniacal water, dried, ignited, and weighed. The filtrate from the ammonium phospho-molybdate is mixed with ammonia, and set for four hours in a warm place, observing if a further yellow precipitate is formed. If this is the case the analysis is defective; the liquid is then neutralised as far as possible with ammonia, more molybdic solution is added, and the second precipitate is weighed along with the former.

The author prepares molybdic solution by dissolving 115 grammes molybdic acid in 460 of ammonia at 0.96 sp. gr., adding 1 litre of water, and pouring this solution into nitric acid of sp. gr. 1.2. The liquid is then allowed to stand for a day and filtered.

For magnesia-mixture he takes magnesium chloride 101·5 grammes, ammonium chloride 200, liquid ammonia 400 grammes (sp. gr. 0·96), and water 1 litre.

Estimation of Manganese in Iron.

The analytical separation of manganese from iron will be found under the heading Manganese, but it may save trouble if there is here given the most trustworthy method of estimating small quantities of manganese when present in metallic iron.

After the silicon is estimated in the iron or steel by Eggertz's method (page 168), the manganese may be estimated in the same amount of material. The filtrate from the silica is diluted with water until it measures 400 c.c. and accurately divided into two portions of 200 c.c. each, one of which is set on one side, and in the other the manganese is estimated in the following manner:—(In the case of wrought-iron and steel, where 8 grammes are taken, the solution is diluted to 200 c.c., and the manganese estimated without dividing the solution). A saturated solution of sodium carbonate is added to the solution until it becomes nearly neutralised, appearing of a deep brown colour; water containing 5 per cent. of sodium carbonate is then added, drop by drop, until a slight turbidity occurs in the solution; and if, on standing in the cold, this turbidity rather increases than diminishes, sufficient carbonate has been added (if too much sodium carbonate has been added, and a precipitate is thrown down, the excess must be neutralised by hydrochloric acid); to the slightly turbid solution add $1\frac{1}{2}$ c.c. of hydrochloric acid, and heat on the water-bath until the solution becomes clear; dilute with about half as much water as the volume of the solution, and add 80 c.c. of a saturated solution of sodium acetate, boil for a quarter of an hour, allow the precipitated iron to settle, and decant the clear liquid through a filter, washing the iron by decantation with boiling water containing $\frac{1}{2}$ per cent. of sodium acetate; finally, throw the iron on the filter, and continue the washing until bromine water gives no reaction, showing that all the manganese has passed through the filter; evaporate the filtrate down to 400 or 500 c.c.; and at the temperature of 50° C. add a few drops of bromine to precipitate the manganese, and keep it near to that temperature for 12 hours, stirring occasionally with a glass rod; the solution after addition of the bromine becomes of a yellow or brownish colour, but should be perfectly colourless before filtering. The manganese is now thrown on a filter which has been dried at 100° C., and accurately weighed, washed with cold water containing 1 per cent. of hydrochloric acid, dried at 100° C., and weighed. The precipitate is a hydrated manganese oxide containing 59·21 per cent. of manganese. The precipitate may also be ignited in a porcelain crucible at a white heat, and is then an anhydrous manganese oxide containing 72·05 per cent. of manganese.

Another method for estimating the manganese is to dissolve 3 or 4 grammes of iron in aqua regia; the solution is largely diluted and filtered, and neutralised with sodium or ammonium carbonate till of a deep brown colour. The iron is precipitated by sodium acetate, and the solution immediately boiled. The bulky precipitate settles quickly; the clear liquid is poured off and filtered. After three washings by subsidence and decantation, the precipitate is thrown on a large filter and again washed. The bulky solution containing all the manganese is evaporated to a small volume and refiltered. The manganese is first precipitated by ammonium sulphide, the sulphide collected and washed with ammonium sulphide water, redissolved in hydrochloric acid, the solution boiled, and the manganese reprecipitated as carbonate by sodium carbonate, filtered off, washed, dried, and ignited till of constant weight.

Mr. J. Spear Parker has discovered that, when copper is also present, this metal is precipitated along with the manganese; and since most specimens of spiegeleisen contain 0.2 or 0.8 per cent. of copper—sometimes 0.5, or even more—the precipitation of the copper with the manganese would seriously impair the accuracy of the determination. In order to ascertain accurately how much copper the manganese would carry down when the usual process of analysis was adopted, the following experiments have been tried:—The finely-divided spiegeleisen, after solution in hydrochloric acid, is peroxidised with potassium chlorate; the excess of chlorine is boiled off, the solution diluted, brought to boiling, neutralised with ammonia, and the iron precipitated by addition of a boiling solution of ammonium acetate (feebly acid). After boiling for an hour, the precipitate is allowed to subside, then filtered and washed with boiling water, the residue dissolved in hydrochloric acid, and the precipitation repeated. The two filtrates are concentrated to a small bulk by evaporation. When copper is present in appreciable amount, this solution has a distinct blue tint. If necessary the solution is again filtered, carefully washed, the filtrate heated, slight excess of ammonia added, and then bromine till the manganese is completely precipitated. After standing for twelve or eighteen hours, the precipitate is filtered; the filtrate is always colourless. The ignited manganese proto-sesquioxide, obtained in this manner from 20 grains of a spiegeleisen containing copper, is dissolved in hydrochloric acid; the solution, which is of a bright green colour, is diluted and transferred to a weighed platinum crucible. A piece of pure zinc is added, and the crucible is almost immediately covered with a copper-red deposit. After complete precipitation of the copper, and solution of the zinc, the liquid is decanted, and the crucible washed several times with boiling water; finally, dried in the water-bath. The copper thus obtained weighs 0.07 gramme. To ascertain how much copper it is possible to precipitate with the manganese, a solution containing copper and manganese sulphates in

equal amount is precipitated with bromine, keeping the solution as nearly as possible neutral. (The precipitate is of a lighter brown when containing copper than the pure hydrated dioxide.) On igniting, it first changes to a fine black colour; after strong and protracted ignition, to brown-black. After weighing, the copper is estimated as before, when it was ascertained that the two metals were present together in the proportion of nearly 1 equivalent of copper to 2 of manganese. The copper can be extracted from the moist precipitate by boiling with strong solution of ammonia, or by digestion with cold dilute sulphuric acid (in the latter case a small portion of manganese also is dissolved). The compound seems to be somewhat unstable; for if, during precipitation, the solution be allowed to become more strongly acid, or if, on the other hand, excess of ammonia be maintained throughout, the proportion of copper is considerably diminished, especially in the latter case.

Two methods may be used to remedy this error: either to separate the copper previous to the precipitation of the manganese, or to estimate the amount of copper in the ignited oxide, and then subtract an equivalent amount of copper oxide from the total weight of the precipitate.

In using the first method, 20 grains of the finely-divided spiegeleisen are completely dissolved in hydrochloric acid, diluted, and a current of sulphuretted hydrogen passed through the liquid. After standing for twelve hours, the solution is filtered and washed with water containing sulphuretted hydrogen; the filtrate is boiled, 10 grains of potassium chlorate added, the iron separated, and the manganese estimated in the usual manner. If the method used be that of estimating the copper in the precipitate, the estimation must be made with the greatest care, on account of the small quantity of copper present; the solution must be decanted immediately the zinc is completely dissolved, and excess of acid must be carefully avoided, otherwise the film of copper will partially redissolve. It is evident that, if the precipitation be effected by ammonium sulphide or sodium carbonate, separation or estimation of the copper is likewise necessary.

Dr. Wolcott Gibbs proposes to precipitate manganese as ammonio-phosphate, weighing as pyrophosphate. This method gives very accurate results in pure solutions, but, in spite of every precaution, a minute amount of copper is carried down with the precipitate in the presence of manganese; it is also liable to the objection that calcium, magnesium, &c., when present, would also be precipitated.

The accurate estimation of manganese in spiegeleisen is of importance commercially; as, being the most important constituent, the value of the material is frequently judged by the percentage of that element alone, while the error introduced by the presence of copper is aggravated by the fact that not only is copper worthless but absolutely injurious in iron.

Estimation of Manganese in Cast Iron.

Sergius Kern dissolves 0·5 gramme of the sample in 15 c.c. hydrochloric acid of sp. gr. 1·12, in a tall glass. At the end of this operation about 0·2 gramme potassium chlorate is added in order to convert all the iron into ferric chloride. If silica is present it is found as a precipitate and filtered off. The liquid then contains ferric and manganous oxides. A solution of caustic potash is added which throws down ferric and manganous hydroxides; to the solution is immediately added 40 to 50 c.c. of a concentrated solution of ammonium chloride, and the whole is boiled for 10 to 15 minutes. The precipitate of hydrated ferric oxide is filtered off and ammonium sulphide is added to the colourless solution. The flesh-coloured precipitate of manganese sulphide is filtered off, quickly washed, placed in a porcelain crucible and heated with sulphuric acid. The manganous sulphate obtained is evaporated to dryness, ignited, and weighed as red oxide containing 72·05 per cent. of manganese. The process is not one of the highest degree of exactitude.

M. Sergius Kern also gives the following method, which, under some circumstances, may be preferable to the one last given:— 0·5 gramme of the specimen in a state of fine powder is intimately mixed with 6 grammes of ammonium chloride in a high platinum crucible, in which the mass is strongly ignited. Then by the following reaction the iron is converted into ferric chloride, which partly flies away and partly sublimes on the cover of the crucible:—



When all the ammonium chloride is decomposed the cover is removed and the sublimed crystals of ferric chloride are washed off from the cover by water. Into the crucible a fresh quantity of ammonium chloride is placed, and the mass is again ignited; this operation is repeated till the sublimation of ferric chloride ceases. The residue is dissolved in 25 c.c. of aqua regia, and then evaporated; the dry mass is mixed with a solution of 10 c.c. of hydrochloric acid in 15 c.c. of water, and the resulting precipitate of silica is filtered off. The filtrate concentrated on a sand-bath is poured into a platinum crucible, in which it is dried, and the resulting mass is next ignited until constant in weight.

The remaining brownish-black compound is mangano-manganic oxide, which is weighed; it contains 72·05 per cent. of manganese.

One gramme of the substance in the form of powder is dissolved in 80 c.c. of hydrochloric acid. The solution is heated during 80 to 40 minutes to allow the chemically-combined carbon to go off in the form of carburetted hydrogen; the liquor is evaporated to the half of the original solution, and water is then added. Silica, if it occurs in the substance, is found as a precipitate; it is filtered from the solution, well washed, and the washing waters are poured into the

solution, to which is added an *excess* of potassium hydrate. In this case the alumina which may be found in the analysed sample remains in solution, and the hydrated ferrous and manganese oxides fall down in the form of precipitates. These oxides are separated from the liquor, washed, dried, and ignited over a strong flame in the presence of air: thus ferric oxide and mangano-manganic oxide are formed. This mixture, in the form of a powder, is introduced into a small hard glass tube, and heated by means of a spirit lamp, whilst a current of pure hydrogen is passed through the tube. In about 15 to 20 minutes the operation is finished; the mass in the tube then commences to be greenish, owing to the formation of manganese monoxide, because, as it is known, the hydrogen reduces the iron oxides to the metallic state, but the manganese oxides only to the state of manganese monoxide. The tube is cooled and the hydrogen is all the time passed over the mass, as the reduced iron, in a finely-divided state, takes fire when exposed to the air. When the tube is cold it is thrown into a metallic cup containing pure naphtha oil. The oil before being used is boiled, in order to free it from the dissolved oxygen of the air. If the residue from the operation cannot be easily separated from the tube, the tube may be broken, and the residue is then carefully powdered under the naphtha and the iron is collected by means of a magnet. The remaining manganese oxide is washed and ignited in the presence of air; the substance turns brown with the formation of mangano-manganic oxide. This is accurately weighed; knowing that mangano-manganic oxide contains 72.05 per cent. of manganese, it is not difficult to calculate the percentage of manganese in the analysed sample.

For estimating manganese in iron and steel, S. Peters dissolves 0.1 gramme pig-iron or steel in 8 or 4 c.c. of nitric acid of 1.20 sp. gr., and boils gently in a long test-tube (about 8 inches long and $\frac{3}{4}$ inch diameter) for 5 or 10 minutes, or until solution is complete. He then adds about 0.2 or 0.8 gramme lead binoxide, and boils again two or three minutes. The tube is cooled in water, the contents filtered through asbestos, and the tube and the residue on the filter washed with distilled water until all the colour has been washed through. Transfer to a graduated tube ($\frac{3}{4}$ inch diameter) holding 50 or 60 c.c., graduated in 0.2 c.c., and compare with a standard solution of permanganate, held in a tube for that purpose. The comparison is made in the same manner as that in the Eggertz method when estimating combined carbon in steel, &c. The solution under comparison is then diluted and well mixed with distilled water (by pouring the contents of the graduated tube into a small dish, and then transferring to the tube again), until its colour is exactly of the same intensity as the standard solution. Having attained to this point, the number of c.c. is noted, and the result is obtained by multiplying each c.c. by 0.00001. Each c.c. is equivalent to 0.01 per cent. manganese when 0.1 gramme of iron is taken for analysis.

For irons containing 0.10 to 0.35 per cent. manganese, 0.1 gramme is the proper quantity; but if there be, say, 0.8 to 1.00 per cent., it is best to take 0.1 gramme and divide the solution (before adding the lead binoxide) into four equal parts, and use 0.25 for the estimation, taking another 0.25 for a second estimation. In case of a high percentage, as 1.00 per cent., if 0.1 gramme is taken the results are too low, on account of some of the manganese escaping oxidation. With an unknown iron one or two trials with 0.1 gramme, or half that quantity, will point out the probable amount, and so be a guide for the next trial. If the amount of iron taken does not yield more colour than corresponds to 25 to 35 c.c. of standard hue, it may safely be said that all the manganese is oxidised. It is well to take this volume as the guide to the quantity of iron to be taken. The quantity of manganese in the liquor to be tested must not exceed 0.4 of a milligramme, and certainly not over half a milligramme. By taking 0.1 gramme of a spiegeleisen, containing nearly 12 per cent. manganese, and diluting to 50 c.c. and taking 2 c.c. or 0.04 for the estimation of the manganese, very nearly the proper amount of manganese was obtained. This seems to show that if the division of the solution can be accurately made, and the bulk of the coloured liquid can be kept down well, the amount of manganese in spiegeleisen can be estimated very fairly.

Combined carbon in large quantity does not interfere with the accuracy of the method, for a steel containing 2.0 per cent. combined carbon, and only 0.8 per cent. manganese, was found to give good results by this method.

The standard is made by diluting a potassium permanganate solution of known strength until each c.c. = 0.00001 gramme manganese.

For example, a $\frac{n}{10}$ solution will contain 8.16 grammes permanganate in 1.0 c.c., or 0.0011 gramme manganese per c.c.; if this be diluted 110 times it will give the required strength. The standard is contained in a tube of the same bore as the one used for the analysis, or else the standard is put in the latter one, and a solution of permanganate put into a tube of nearly the same bore, and diluted until it exactly corresponds with the standard solution, when it will serve as a standard.

Permanganic acid of the proper hue keeps better than potassium permanganate of the same hue, and is easily made by adding nitric acid to the latter. The time occupied in obtaining a result by this method is about half an hour.

M. C. Stoeckman finds that iron and manganese cannot be completely separated by a single precipitation. Some manganese always remains along with the iron. It is therefore necessary, after having filtered and washed several times, to redissolve the ferric oxide, and to reprecipitate with sodium acetate. Even two precipitations do not suffice for absolute accuracy. As regards phosphorus, the differences

in the results are due to the fact that some chemists dissolve the ore in nitric acid, and others in aqua regia, the quantity found being lower in the latter case. The author's procedure is as follows :—5 grammes of pulverised spiegeleisen are dissolved in 60 c.c. of pure nitric acid of sp. gr. 1·2, in a glass beaker capable of containing 800 to 1000 c.c., and which is covered with a watch-glass. The acid is added by degrees. When the mixture ceases effervescing the beaker is set on the sand-bath, so as to bring the contents to a boil. The substance is dissolved in ten minutes at the most, and the solution is then decanted into a porcelain crucible of 200 c.c. capacity, and evaporated to complete dryness on the sand-bath, covering with a watch-glass to prevent spiriting. The crucible is then covered with a porcelain lid, and it is carefully heated over the lamp ; the lid is then removed, and the heat is raised till all organic matter is burnt off, or at least decomposed. When completely cold, concentrated hydrochloric acid is added, and the crucible, covered with a watch-glass, is heated on the sand-bath till everything is dissolved. The liquid is then filtered into a beaker, and evaporated to approximate dryness, mixed with a little ammonia until the iron oxide is thrown down, and then again with nitric acid till all is redissolved, boiling if needful. When quite cold, 50 to 60 c.c. of molybdenum mixture are added, and it is allowed to stand from 12 to 24 hours at a temperature of 80°.

Mr. Riley makes the following remarks on the estimation of manganese in spiegeleisen, etc. There are two methods now in use :—
(a) *The direct method.*—The pulverised spiegeleisen (about 1 gramme) is dissolved in dilute nitric acid, sp. gr. 1·2, a little potassium chlorate and hydrochloric acid added to destroy the soluble organic matter from the combined carbon ; the solution, diluted to about a litre, is neutralised with sodium or ammonium carbonate, and sodium or ammonium acetate added, the solution boiled, the basic iron peracetate allowed to settle, and filtered off. This precipitate is redissolved in hydrochloric acid, and the process repeated to ensure complete separation of the manganese. The filtrates are evaporated to 1½ litre, allowed to cool, 2 to 4 c.c. bromine added, the solution well shaken, ammonia sp. gr. 0·88 added in excess, the solution heated gradually for an hour, boiled for a few minutes, the precipitate allowed to settle, filtered (the filtrate should be evaporated and tested for manganese), dried, and ignited in a muffle or over a gas-blowpipe for half an hour. (b) *The indirect method.*—The finely-powdered spiegeleisen (about 1 gramme) is dissolved in dilute sulphuric or in hydrochloric acid, the liquid diluted with recently-boiled, cooled, distilled water, and the iron estimated volumetrically ; to the percentage of iron thus obtained 5 per cent. is added for carbon and impurities, and the difference is assumed to be manganese. The results obtained by this method are usually too low, from the formation of soluble organic matter during the process of solution. This error can be obviated by using nitric acid for a solvent, evaporating to dryness

and heating; the iron and manganese oxides are then dissolved in hydrochloric acid, the solution largely diluted, and reduced with sodium sulphite. Results obtained thus agree very closely with the direct method. The author gives 14 analyses, showing that the addition of 5 per cent. for impurities to the percentage of iron is a fair one. Thus, for all practical purposes, the indirect method is sufficiently accurate, and can be accomplished in one hour, the direct requiring five or six hours. The author strongly recommends the use of ammonium carbonate and acetate instead of the corresponding sodium salts in the direct method, and proves, by check experiments with pure manganese sulphate, &c., the statements of Fresenius and others, that the presence of ammoniacal salts prevents the complete precipitation of manganese by bromine and ammonia, to be erroneous. On the other hand, if sodium salts be used, the ignited precipitate will contain soda. The author considers that sulphur cannot exist in spiegeleisen. He estimates the carbon by dissolving the iron in neutral copper chloride, and after complete solution of the iron and precipitated copper the carbon is filtered on asbestos, and burnt with copper oxide in a current of oxygen; the carbon estimations by the colour test are unsatisfactory for high percentages of carbon. According to the author, the percentage of carbon varies with the percentage of manganese.

Estimation of Manganese in Manganiferous Iron Ores.

These ores contain baryta; many contain zinc oxide and some potash or soda in appreciable quantities. The use of ammoniacal salts prevents any large error from the presence of the zinc oxide, but it is difficult to get rid of the baryta; even in the presence of sulphuric acid it remains in combination with the manganese, and is precipitated with it unless special precautions be taken. Lime, if present, may also be precipitated with the manganese. After insisting on the importance of taking fair samples, and of estimating all the constituents directly, the author gave the following process as one which yielded the best results:—1 gramme of the ore dried at 100° C. is dissolved in hydrochloric acid, the siliceous matter separated by filtration, and the larger portion of the free acid driven off. The liquid is made up to about $\frac{1}{3}$ of a litre, and allowed to stand for four hours, after adding a few drops of sulphuric acid to separate any baryta. The solution is now diluted to about 1 litre, neutralised with ammonia after the addition of ammonium acetate, boiled, allowed to settle, and filtered; the unwashed precipitate is redissolved in hydrochloric acid, and again precipitated with ammonia and ammonium acetate. The basic iron peracetate, after settling, is filtered off and washed three or four times with boiling distilled water, containing a few drops of ammonium acetate. The filtrate is evaporated to $1\frac{1}{2}$ litre, when cold, 2 to 4 c.c. of bromine are added, and the process completed as described above. After ignition the precipitate should be dissolved in a

small quantity of hydrochloric acid, the residue, if any, filtered off, a drop of sulphuric acid added, and the precipitate, if any occurs, separated. It is most important to test the ignited Mn_2O_3 for impurities, baryta, zinc, lime, &c. Chlorine can be substituted for bromine, but without advantage. The ammonium sulphide process, the author considers to be most objectionable.

F. Kiesser says that one of the main causes of the loss of manganese in these estimations springs from the employment of too large an amount of sodium acetate in the previous precipitation of the iron. The author finds that in a perfectly neutral solution 1 gramme of sodium acetate suffices to precipitate completely 1.1 gramme of iron in 500 c.c. of solution, and even in the presence of 1 gramme of acetic acid. When the estimation of the manganese alone is required, he cools the liquid, makes up its volume to 500 c.c., filters, and estimates the manganese in 250 c.c.

The following process is recommended by T. Rowan as superior for speed and accuracy to the other processes commonly resorted to, where manganese in quantity has to be estimated:—

A convenient quantity of the sample, say 20 grains, in as fine a state of division as possible, is digested in a long-necked flask, with about $1\frac{1}{2}$ ounce of hydrochloric acid, until complete solution is effected. The solution is then oxidised with potassium chlorate added from time to time, and finally boiled until traces of chlorine can no longer be detected.

The solution is now neutralised by a solution of sodium carbonate added in small successive quantities, the flask being well agitated after each addition of the alkali. On nearing the neutral point, each addition of the sodium carbonate occasions the separation of small quantities of iron and manganese carbonate, which disappear on the flask being shaken. When this is observed, the alkali must be added with extreme caution, but the deep blood-red colour now acquired by the solution will, after a little practice, be a sufficient indication to the operator that the desired point of neutralisation has been attained. Or, if it is preferred, the smallest excess of sodium carbonate may be added, and the permanent precipitate which forms redissolved by the cautious addition of hydrochloric acid, introduced drop by drop.

Before treating with sodium carbonate, the solution should be evaporated to as small a bulk as possible, the presence of much free acid causing the expenditure of an unnecessary amount of alkali, and the violent effervescence caused by escaping carbonic acid often entails loss by the projection of portions of the solution from the flask.

From 6 to 8 ounces of water are now added, and the iron precipitated as the basic iron acetate by the addition of a concentrated solution of sodium acetate.

If the solution has previously been successfully neutralised with sodium carbonate, the ferric acetate will at once make its appearance;

but if that point has not been reached, the iron will only precipitate after boiling, and then not completely, and the precipitate will be found to be so gelatinous as to cause much trouble by clogging the filter.

After the addition of the sodium acetate, the flask and contents are briskly boiled for about 20 minutes, and then allowed to repose for a few minutes, so that the iron acetate may settle to the bottom of the flask, when the solution is carefully decanted from it on a filter. More water is then added to the flask, with a few drops of sodium acetate, boiled for five or six minutes, and again decanted from the precipitate. This is repeated a third time. The iron acetate can then be thrown on the filter and washed with boiling water. The filtrate, with washings, is removed to a beaker and brought to a temperature of about 100° F., and a stream of chlorine gas passed through until a faint smell of that gas can be detected from the liquid. This is ascertained by stopping, from time to time, the passage of the chlorine, blowing from the surface of the liquid in the beaker the gas that may have lodged there, and then testing by the smell. If chlorine can be detected the addition of the gas is finally discontinued. The beaker is now carefully covered and set aside in a moderately warm place for six hours. The precipitated manganese binoxide is removed by filtration, and chlorine is again passed through the filtrate to ascertain whether all the manganese has been removed. When the precipitated manganese settles to the bottom of the beaker, if the liquid above is purple-coloured it indicates that an excess of chlorine has been used, and that permanganic acid has been formed. This is easily remedied, as the permanganic acid is at once reduced to the binoxide by the presence of any organic matter. A few drops of alcohol may be added, and the precipitated manganese binoxide filtered off.

The precipitated manganese binoxide is redissolved by pouring hot dilute hydrochloric acid on the filter. The manganese is reprecipitated as carbonate by a solution of sodium carbonate and boiled well to expel all carbonic acid, the manganese carbonate being slightly soluble in carbonic acid. The manganese carbonate is then collected on a filter, washed well with boiling water, dried, ignited, and weighed as the red oxide.

The manganese binoxide has such a tendency to fix alkali, that it cannot be directly ignited to the red oxide. When this is done without redissolving and reprecipitating as carbonate, 1 part of the ignited precipitate contains 0.0842 of alkali, which must be deducted from the weight before calculating the percentage of metallic manganese.

In a rigorous analysis, however, it will be found more satisfactory to proceed as directed above, namely, redissolve the manganese binoxide first obtained, and reprecipitate as carbonate before proceeding to ignite and weigh. The amount of metallic manganese is readily ascertained from the weight of the ignited red oxide, 100 parts of which contain 72.05 parts of metallic manganese.

Estimation of Basic Cinder and Oxides in Manufactured Iron.

The principal value attached to determinations of slag and oxides in defective iron is the almost absolute certainty of discovering whether to the chemical constituents of the metal or to its careless manufacture may be attributed the faults observed. When we contrast the 'life' of an iron rail of fair chemical purity with that of 'mild' steel rails of nearly the same composition, it is forcibly suggested to even the most superficial observer that the duration of a rail is proportionate to the cohesion of its metallic particles, due principally to freedom from mechanical impurities.

Mr. W. Bettel estimates the cinder, &c., by the following method. It only occupies an hour or so, and has the advantage of yielding constant results:—5 grammes of the borings are heated with a solution of 10 c.c. bromine and 85 grammes potassium bromide in 150 c.c. water. Heat is continued until the iron is dissolved, the solution filtered through a 4" Swedish paper (previously washed with hydrochloric acid and boiling water), drained and washed with a solution of sulphurous acid containing 5 per cent. hydrochloric acid. When the filtrate is practically free from iron, wash with boiling water containing $\frac{1}{2}$ per cent. hydrochloric acid, then with pure water rinse into a small platinum dish, evaporate to low bulk, and dissolve out silica by means of a hot solution of sodium carbonate. Boil, dilute, filter, wash with hot water, then with a $\frac{1}{2}$ per cent. solution of hydrochloric acid, and finally with water. Dry, ignite, and weigh. Estimate the silica in the residue in the ordinary manner. The bromine in the first filtrate may be recovered as potassium bromide in an obvious way.

Some analysts object to the bromine process on account of the vapour contaminating the air of the laboratory. To those Mr. Bettel recommends the following process, which has given good results:—5 grammes of the iron, rather finely divided, are dissolved in 60 c.c. clear solution of cupric chloride (1 in 2), mixed with 100 c.c. saturated solution of potassium chloride. When no particles of iron can be felt by the aid of a glass rod, add 50 c.c. of dilute hydrochloric acid (1 in 20), boil, and filter through a 4" Swedish paper (previously moistened with hot hydrochloric acid [1 in 8], then with saturated solution of potassium chloride). Wash the residue on the filter with potassium chloride solution till all the copper is removed, then with hot dilute hydrochloric acid (1 in 50), finally with hot water. Separate the silica as before, ignite, and weigh. If the copper obstinately adheres to the paper, as sometimes happens, slip over the tube of the funnel a piece of indiarubber tubing with clip (or plugged with glass rod), fill up funnel with strong liquid ammonia, cover, and allow to remain for half an hour, then proceed with dilute acid, &c., as before.

The results of both processes agree with Fresenius's galvanic method.

Estimation of Titanium in Iron.

The detection of titanium in iron is easy, although its estimation is very difficult. Many methods have been tried in the author's laboratory, but none appear perfectly satisfactory. The best results have been obtained by following Riley's plan.¹ This is essentially as follows:—A weighed portion of the iron borings is treated with fuming nitric acid in a flask, a few drops of hydrochloric acid added from time to time, the whole being well boiled. The contents of the flask are then transferred into a porcelain dish, evaporated to dryness, and heated strongly. On cooling, it will be found that the iron oxide readily detaches itself from the dish, and can be easily transferred into a beaker, the portions left on the dish being dissolved in hydrochloric acid, and poured on the contents of the beaker; the dish may be rinsed out, if necessary, with strong hydrochloric acid. The contents of the beaker are boiled for from two to three hours, until complete solution of the iron is effected; and as some quantity of hydrochloric acid is required for this, the best plan is to allow a large portion of the excess of acid to evaporate in the beaker, retaining only as much as is requisite to keep the iron in solution. The silica is filtered off in the usual way, after diluting with water and adding a few drops of hydrochloric acid on the filter, to dissolve the basic salt formed by the water. By this means the silica can be obtained nearly white after burning off the graphite, and very little iron will be found with it unless much phosphorus be present, as the silica invariably contains more or less iron phosphate from the insoluble iron phosphide, which cannot be completely dissolved out by hydrochloric acid. Before determining the titanium, the residue from the silica should be fused with potassium bisulphate, dissolved in water, and added to the solution of iron in which the titanium is to be determined. The solution is reduced with sodium sulphite, and the excess of sulphurous acid is driven off by boiling. The solution is then nearly neutralised with ammonia, and ammonium or sodium acetate added; if there is only a small quantity of phosphoric acid, there will always be sufficient iron peroxide to precipitate it, but if not, a few drops of nitric acid must be added so that the precipitate produced is distinctly red, and the solution boiled and filtered as quickly as possible. The residue is fused with potassium bisulphate, or, where nitric acid is used, this is driven off with sulphuric acid. The result of the fusion with potassium bisulphate is dissolved in cold water (when a little iron phosphate, which remains insoluble, is separated), boiled for some hours, and allowed to stand a night in a warm place, when the titanous acid is filtered off and washed with dilute sulphuric acid, dried, ignited, and weighed.

The above process is not very satisfactory for the quantitative

¹ *Chemical News*, viii. 226, 283.

determination of titanitic acid. The iron phosphate (insoluble in the potassium bisulphate) cannot be washed without its passing through the filter, and very frequently, also, the small amount of iron keeps up the titanitic acid, as iron even in small quantities has a very great effect in preventing the precipitation of titanitic acid, so that it is always advisable to add a little sodium sulphite, which reduces the iron oxide and facilitates the precipitation of the titanitic acid.

Titanium may, however, be found more satisfactorily and more readily, during the process usually adopted to determine the amount of graphite in pig-iron, provided a large quantity of the pig be operated on. About 200 grains of the pig are to be dissolved in dilute hydrochloric acid; when the pig is nearly all dissolved, and the action of the acid has ceased, more hydrochloric acid is added, and the solution well boiled, so as thoroughly to extract all the iron. The solution is then thrown on dried counterpoised filters encircling each other, and the filter well washed to remove all the iron. It is then treated with dilute potash, and washed once; then re-treat with it, so as to entirely remove the silica. The potash is thoroughly washed out, and the filter treated with hydrochloric acid, thoroughly washed and dried at 250° F. until the weight is constant. This gives the graphite, on burning which a residue of a dirty light brown colour is left, which, fused with potassium bisulphate and subsequent treatment as above explained, is seen to be nearly pure titanitic acid.

Mr. Tosh advises the approximate estimation of titanium in iron to be effected in the following way:—About 6 grammes of iron are dissolved in hydrochloric acid, and the whole evaporated to dryness. The dried mass is moistened with hydrochloric acid, water added, and the solution filtered. Part of the titanium exists in solution (*a*) and part in the insoluble residue (*b*). The solution, if containing much iron perchloride, is reduced by sodium sulphite, the excess of sulphurous acid boiled off, a little iron perchloride added, and the titanitic acid precipitated in combination with the iron sesquioxide thus introduced, by means of sodium carbonate, as in the estimation of phosphorus. The small precipitate is quickly filtered off, washed, dried, ignited, and carefully set aside. From the insoluble matter (*b*) graphite is burned off, and the silica is removed by hydrofluoric acid in the presence of sulphuric acid. To the residue after this treatment the small ferruginous precipitate from (*a*) is added, and the whole fused with potassium bisulphate. When cool, the fused mass is extracted with cold water, and from the clear filtered solution titanitic acid and iron are precipitated by ammonia; the precipitate is slightly washed, and ammonium sulphide added. The iron sulphide thus formed is dissolved by sulphurous acid, while the titanitic acid mixed with sulphur is left undissolved, and may be collected, ignited, and weighed, after which it should be tested as to its purity.

Titanium may also be estimated by loss according to the following

plan devised by Riley, but this estimation is not so satisfactory as a direct estimation, and the results obtained are probably a little high:—About 15 or 16 grains of the iron are dissolved in nitro-hydrochloric acid, and the solution evaporated to dryness, the silica separated in the usual way, and volatilised with hydrofluoric and sulphuric acids, the residue fused with a little potassium bisulphate, dissolved in cold water, and added to the filtrate from the silica. The solution is precipitated with sodium or ammonium acetate, first nearly neutralising it with ammonia; after boiling well, the basic iron peracetate is filtered off and well washed, adding occasionally a drop or two of the alkaline acetate. The precipitate is then dissolved in hydrochloric acid, and the iron peroxide precipitated by ammonia, filtered, dried, and ignited in the usual way. The iron peroxide is then dissolved in hydrochloric acid, and, the small amount of silica present separated, the solution is reduced with sodium sulphite, and the iron estimated with a standard solution of potassium bichromate. This will give the percentage of pure iron peroxide: and the difference between the iron peroxide weighed and that estimated by standard solution is considered to be titanous acid and phosphoric acid. The phosphoric acid having been estimated by another distinct operation, the amount present in the iron peroxide is calculated and deducted from the above difference—the remainder being considered to be titanous acid, from which the percentage of titanium in the iron is calculated.

In testing a siliceous residue for titanous acid with hydrofluoric acid it must be remembered that a titanium fluoride is formed at the same time, which cannot be heated without the larger portion going off. Riley¹ describes an experiment in which 2·235 grammes of titanous acid exposed (with the occasional addition of water) for twenty-four hours to the action of hydrofluoric acid in Brunner's apparatus, until it was completely dissolved, left, on evaporating to dryness and heating carefully to a low red heat, a residue of only 0·99 gramme, which still contained a trace of fluorine. Hence it follows that residues obtained by this method only represent a portion of the titanous acid actually present.

In estimating the amount of titanium or titanous acid in samples of cast or wrought iron, this substance has usually been sought for in the residue insoluble in acids, but, according to the following experiments of Mr. Forbes, such a procedure cannot be relied upon as furnishing correct results.

A sample of cast-iron produced from smelting a titaniferous magnetite from Gullaxrud, in Norway, in a charcoal blast-furnace, was taken, and 251·59 grains in small fragments dissolved in nitro-hydrochloric acid; the insoluble residue was collected on a filter, incinerated, digested with sulphuric acid, and the titanous acid present estimated as described at page 197, when it was found to amount to 0·52 grain, equivalent to 0·207 per cent. titanous acid, or 0·126 per cent. titanium.

¹ *Journ. Chem. Soc.* xii. 13.

The filtrate was now neutralised carefully with ammonia, and then a slight excess of ammonia added, so as to cause a small permanent precipitate of iron sesquioxide to be formed, which was then filtered off from the ferruginous solution, and washed. This precipitate, which contained all the titanic and phosphoric acid present in the iron, along with an excess of iron sesquioxide, was now dissolved in a little very dilute sulphuric acid, some nitric acid added, and the solution boiled: an immediate precipitate of titanic acid was formed, which, when estimated, amounted to 0.14 grain, or 0.056 per cent., equivalent to 0.084 per cent. titanium. The examination of this cast-iron resulted in showing that it contained 0.207 per cent. titanic acid in the insoluble form, and 0.056 per cent. titanic acid in the soluble form, or a total of 0.623 per cent. titanic acid; and that, consequently, more than 20 per cent. of the entire titanic acid had been dissolved by the acids employed in the analysis.

Another sample of cast-iron was also examined with the same object in view. In this case 104.26 grains of the cast-iron in fragments were dissolved in nitro-hydrochloric acid, and left an insoluble residue which, after incineration, weighed 2.47 grains; this was, as in the last case, digested in concentrated sulphuric acid; the titanic acid, which was estimated as before described, weighed only 0.02 grain. The acid filtrate was then treated with ammonia, so as to precipitate a small amount of the iron sesquioxide along with any titanic acid contained in the iron, and this latter estimated, as in the former case, amounted to 0.03 grain.

The result of this experiment shows, therefore, that this cast-iron contained a total of only 0.048 per cent. titanic acid, of which 0.019 per cent. remained in the insoluble residue, whilst 0.029 per cent. had been dissolved in the acid solution, confirming the conclusion previously arrived at, that when a very small amount of titanic acid is present in a substance, the major part of it is often, if not always, to be found in the solution, and not in the insoluble residue.

Estimation of Titanic Acid in Titaniferous Iron Ores.

Mr. W. Bettel proposes the following modification of Mr. D. Forbes's process:—

Fuse about 0.5 gramme of the finely powdered ore with 6 grammes of pure potassium bisulphate (which has been recently fused and powdered) in a platinum crucible at a gentle heat, carefully increased to redness, and continued till the mass is in tranquil fusion.

Remove from the source of heat, allow to cool, digest for some hours in 5 or 6 ounces of cold distilled water—not more than 10 ounces are to be used, as it generally causes a precipitation of some titanic acid—filter off from a little pure white silica, dilute to 45 or 50 ounces, add sulphurous acid until all the iron is reduced, then boil for six hours, replacing the water as it evaporates.

The titanic acid is precipitated as a white powder, which is now to

be filtered off, washed by decantation, a little sulphuric acid being added to the wash-water to prevent it carrying away titanous acid in suspension. Dry, ignite, allow to cool, moisten with solution of ammonium carbonate, re-ignite and weigh. The titanous acid is invariably obtained as a white powder with a faint yellow tinge, if the process has been properly carried out.

For special methods for the detection of sulphur, phosphorus, silicon, titanium, &c., see the chapters treating on these elements, and on Silicates.

EXAMPLES OF THE ANALYSIS OF IRON, STEEL, AND IRON ORES.

In the preceding pages we have given methods for the detection and estimation of the carbon, sulphur, phosphorus, and other elements associated with commercial iron and steel. When these are required to be estimated in the same specimen of metal or ore, some of the methods can be materially shortened, as will be seen by the following examples of methods for the complete analysis of iron, steel, and iron ores which have been selected in illustration.

Analysis of Blister Steel.

Mr. David Forbes gives the following particulars¹ of the analysis of blister steel converted in Sheffield from bar iron of Swedish manufacture. The portion selected for examination was obtained in a sufficiently divided state by chipping off the bar with a cold chisel, since it was found that no reliance could be placed on filings, which, even if produced by the best files, were always contaminated by the *débris* of the file itself. The estimation of the constituents was made as follows:—

Estimation of the Total Amount of Carbon.—77·91 grains of the steel, in the form of such chippings, were allowed to remain for about ten days in a cold solution of 200 grains of pure copper chloride until no undissolved steel remained; the residue was then well washed by decantation, dried, mixed with 100 grains of pure copper oxide, and burnt in a current of purified dry oxygen gas, at a heat sufficient to soften the Bohemian glass tube. The carbonic acid, collected, as usual, in a potash apparatus, amounted to 2·08 grains, or equivalent to 0·729 per cent. of carbon in the steel.

Estimation of the Sulphur.—107·58 grains were placed in a flask provided with a safety-funnel, and digested for twenty-four hours in the cold, with strong hydrochloric acid; the gas evolved was passed through a solution of pure zinc chloride supersaturated with ammonia: the iron being all dissolved, the zinc solution was boiled with nitric acid in some excess, nearly neutralised by ammonia to pre-

¹ *Chemical News*, xvi. 105.

vent any solvent action from excess of acid, and precipitated by a solution of pure barium chloride—0·04 grain barium sulphate was obtained, equivalent to 0·005 per cent. sulphur in the steel.

Estimation of the Silicon and Uncombined Carbon.—The solution from the above was evaporated in a water-bath to dryness, redissolved in water with some hydrochloric acid, and filtered from the insoluble silica and graphite; these latter were washed off the filter into a silver basin, in which they were boiled with potash, which dissolved out the silica, leaving the graphite, which was collected on a filter, washed, dried, carefully scraped off the filter, and dried at 250° F.; it weighed 0·11 grain, equivalent to 0·102 per cent. uncombined or graphitic carbon. The potash solution of silica was supersaturated with hydrochloric acid, evaporated to dryness, and the residue treated with water rendered acid by hydrochloric acid. The silica was then filtered off and estimated as usual, being 0·06 grain, or equivalent to 0·0804 per cent. silicon in the steel.

Estimation of the Manganese.—The acid filtrate, after separating the graphite and silica by filtration, was now nearly neutralised by ammonia, and then treated with barium carbonate in excess, filtered, and the filtrate precipitated by ammonium sulphide. The manganese sulphide mixed with some barium sulphate was then treated with weak sulphuric acid, filtered, and the manganese precipitated by sodium carbonate, affording 0·18 grain manganoso-manganic oxide, or equivalent to 0·12 per cent. manganese in the steel.

Search for Phosphorus.—52·75 grains of the steel treated precisely according to Abel's directions,¹ afforded no trace of magnesium ammonio-phosphate. 78·28 grains examined by Spiller's process¹ gave the same negative result; and, lastly, 48·07 grains tested by Eggertz's method by ammonium molybdate¹ did not afford any trace of phosphorus.

Estimation of Iron.—The amount of iron present was estimated as loss. The percentage results were as follows:—

Carbon combined	0·627
" graphitic	0·102
Silicon	0·030
Phosphorus	—
Sulphur	0·005
Manganese	0·120
Iron	99·116
							<hr/> 100·000

Analysis of Magnetic Iron Ore.²

The iron ore here under consideration was strongly attracted by the magnet, and, with the exception of traces of iron pyrites and

¹ See chapter on Phosphorus.

² By Mr. Forbes (*Chemical News*, xvi. 259).

pyrrhotine, all the iron was present in the state of magnetic oxide (magnetite). The percentage of metallic iron, besides being calculated from the amount of iron sesquioxide obtained in the course of the analysis, was also estimated in a separate portion of the ore by the potassium bichromate volumetric process, after its previous solution and reduction to the state of protoxide by metallic zinc: the oxygen combined with the iron was estimated from the loss in analysis. The portion of the mineral employed for estimating the amount of sulphur was dissolved in nitro-hydrochloric acid, filtered from the insoluble siliceous matter, and the filtrate evaporated nearly to dryness in a water-bath, so as to expel the excess of free acid (which otherwise might augment the solubility of the barium sulphate), and after having been precipitated by barium chloride, the barium sulphate was estimated as usual. Phosphorus was sought for in a larger amount of the ore, both by Abel's and Spiller's processes, and also by the molybdate process. The manganese was separated from the iron by barium carbonate, and the other constituents, carbonic acid, calcium, magnesium, and aluminium, determined as usual.

Analysis of Spathic Iron Ore.

Professor Wöhler gives the following process for the analysis of spathic iron ore:—Dissolve a weighed quantity of the finely-ground ore in hydrochloric acid, to which is added a little nitric acid or potassium chlorate. Precipitate with ammonia, but be careful not to filter until the liquid has been boiled till all odour of ammonia has disappeared; the iron precipitate then contains no trace of calcium, magnesium, or manganese. The liquid containing no trace of free ammonia, the filtration may be performed in contact with air. The filtrate must be concentrated by evaporation, and the three bases which it contains precipitated with an excess of potassium carbonate, continuing the ebullition so long as no ammonia is disengaged. Filter the liquid and redissolve the precipitate in nitric acid, then evaporate to dryness, and carefully heat to dull redness. Dilute nitric acid will then separate the lime and magnesia from the insoluble manganese oxide.

Analysis of Titaniferous Iron Ore.

The composition and metallurgy of titaniferous iron ores (Norwegian) received great attention from the late Mr. David Forbes, whose experience in this subject dates from 1847. The following is his process for analysing them:—A weighed amount of the ore is fused in a gold crucible with eight times its weight of sodium bisulphate, until all soluble matter has been taken up. The fused mass is treated with cold water until nothing remains but some pure white silica, which is filtered off, washed, and estimated; to the solution, much diluted with water, a few drops of nitric acid are added (in order to prevent

the titanio acid carrying down iron sesquioxide along with it), and the whole boiled for a considerable time. The titanio acid thus precipitated is estimated after ignition, when it possesses a light yellow colour. The aluminium, iron, calcium, and magnesium in the filtrate are now separated as usual, and the estimation of the iron checked by the volumetric process (by potassium bichromate) upon a separate portion of the ore dissolved in nitro-hydrochloric acid, and also used for estimating the amount of sulphur present. If phosphorus is present, it is separated by fusion with sodium carbonate, and afterwards estimated as magnesium pyrophosphate in the usual manner.

Immediate Analysis of Meteoric Iron.

The numerous researches hitherto made with regard to the composition of meteoric irons, have demonstrated the existence of the following compounds in these extra-terrestrial bodies :—

1. The *general mass*, which is formed by the union of several alloys in which iron and nickel are predominant, and which we will designate under the name of *nickeliferous iron*. Among the substances comprised in this mass, *kamacite*, *ténite*, and *plessite* are specially noticeable.

2. The *carburetted iron*, comprising *campbellite* and *chalypite*, recognisable by the carboniferous deposit which they give under the action of acids.

3. *Sulphuretted iron*, or *troilite*, which appears in nodules and in veins.

4. *Iron and nickel phosphide*, or *Schreibersite*.

5. *Graphite*.

6. *External crust*.

7. *Stony particles*, or *crystals*.

8. *Gases* retained by occlusion.

9. Several compounds which are only met with exceptionally, as *chromite* and *iron protochloride*.

(The last may indeed have a terrestrial origin, according to the opinion of Mr. Shepard.)

M. Stanislas Meunier, Aide Naturaliste at the Museum of Paris, has tried to separate these different substances, and has submitted each of them to a special examination. His experiments, which have resulted in fixing their chemical formulæ, were communicated to the *Chemical News* for January, 1869, and are given in abstract in the following pages.

I. Nickeliferous Iron.—The first problem to be solved is the separation of the different alloys which are mixed in the general mass of meteoric irons; but it is necessary first of all to prepare that general mass free from other substances already named. For this end, the iron being reduced to powder by means of a hard file, the metal is thrown

into pure potash, in a state of fusion, in a silver crucible. Instantaneously the alkali, hitherto limpid, becomes turbid, owing to the presence of little grey flakes, which consist of iron oxide and are the result of decomposition of troilite, schreibersite, stony matters, &c.

When this decomposition of foreign substances is complete, the alkaline mass is cooled and treated with water. All the potash is washed away with the greater part of the iron oxide. The remainder of this oxide is easily dissolved by strong nitric acid, in which the metallic iron becomes passive. The metallic powder is then well washed and dried; it is formed exclusively of nickeliferous iron, containing, however, in certain cases, a small proportion of carburetted iron.

Chemical methods have not yet completely succeeded in separating the alloys mixed in the nickeliferous iron, and, after several attempts, M. Meunier was obliged to have recourse to physical processes. His experiments have been made with the meteoric irons of Caille (France), and of Charcas (Mexico).

It was necessary, first of all, to estimate with accuracy the number of constituent compounds contained in the nickeliferous iron of these masses. For this purpose a small polished plate of the iron of Caille was carefully and uniformly heated. This operation, of which the first idea is due to Widmanstätten, drew, by the unequal oxidation of the different immediate principles, a yellow net upon a blue ground. There were also several portions of an intermediate colour, clearly limited like the others, and occupying the spaces bounded by the crossing of the yellow lines. An attentive examination showed that the three metallic compounds were reducible to two; the third being formed by the mixture of the others, reduced to alternate thin sheets. The blue colouration is formed by kamacite, and the yellow by ténite.

Their separation was very difficult, on account of the analogy of the chemical properties of the two minerals. Although it is true that kamacite is more soluble than ténite (and this is proved by the experiments of Widmanstätten), this difference is too small to permit of a separation. When all the kamacite is dissolved, only a very small proportion of ténite remains, the greatest part being dissolved also.

To effect the separation, some metallic powder was heated upon a glass plate. The particles formed by kamacite became blue, whilst the particles of ténite were yellow. The two sorts of grains were then separated with pincers. After about fifteen operations, 2 grammes of kamacite and 0.5 gramme of ténite, were collected fit for chemical examination. The Charcas iron gave the same results.

The specific gravity of ténite is 7.880. Its analysis yielded the following numbers:—

Iron	85.0
Nickel	14.0
	<hr/>
	99.0

which agree with the formula Fe_8Ni .

Kamacite has a specific gravity of 7.652, and its composition was found to be—

Iron	91.9
Nickel	7.0
	<hr/>
	98.9

Agreeing with the formula Fe_{14}Ni .

On this subject it will be remarked that, admitting, according to the numbers given above, that the Caille iron contains 80 per cent. of kamacite and 20 per cent. of ténite, its elementary formula will be expressed by



which gives numbers very near those which M. Rivot obtained in the elementary analysis of that mass.

The above formula gives—

Iron	91.4
Nickel	8.6
	<hr/>
	100.0

Whilst M. Rivot found, in two analyses—

Iron	92.3	92.7
Nickel	6.3	5.6
	<hr/>	<hr/>
	98.6	98.3

All meteoric irons are not so simple as those of Caille and of Charcas. There are some which contain, with kamacite and ténite, a certain quantity of other metallic alloys. One of the most important of these is plessite, which abounds, for example, in irons of Jewell Hill (North Carolina) and of Oldham (Kentucky). This has been isolated by the same method which served for the preceding substances. Plessite has a density of 7.85, and its composition appears to be satisfactorily represented by the formula Fe_{10}Ni .

Amongst the other alloys of iron and nickel may be mentioned *octibbehite*, whose composition is exceedingly remarkable, owing to the large proportion of nickel (59.6 per cent.) it contains. Its density is only equal to 6.854. The meteoric iron of Octibbeha (Mississippi) seems to be entirely formed of that alloy, according to the researches of Mr. Taylor.

II. Carburetted Iron.—Several meteoric irons give, by the action of acid, a black deposit, more or less abundant, consisting of carbon. This carbon comes from a compound whose position is analogous to that of steel. In this point of view, the meteoric iron of Campbell (Tennessee) may be specially mentioned. It gives, on analysis, a metallic substance, formed by the union of 1.5 per cent. of carbon with 97.54 per cent. of iron. For it the name of *campbellite* may be proposed; its density is 7.05. Mr. Shepard gives the name of *chalypite*

to an iron carbide which Forchhammer has detected in the meteoric iron of Niakornak (Greenland), and of which the formula is CFe_2 .

III. **Sulphuretted Iron.**—To prepare the sulphuretted iron, or *troilite*, in a complete state of purity, we may have recourse to the metallic powder. This powder is placed for a quarter of an hour in a boiling concentrated solution of copper sulphate. All the nickeliferous iron is dissolved, and, by decanting and washing, a mixture of metallic copper, troilite, schreibersite, graphite, and stony matter may be obtained.

A small quantity of concentrated nitric acid dissolves the copper. The magnet, acting under water, is the best means to separate troilite and schreibersite (which are magnetic) from graphite and stony matter. Finally, lixiviation can be employed to separate troilite from schreibersite.

When the iron under experiment contains only a small quantity of troilite, it is preferable not to use nitric acid, which always dissolves a little of the desired substance. In such cases the nickeliferous iron may be dissolved by means of mercury bichloride. The mercury protochloride is carried off by a solution of chlorine, and it is easy to separate the metallic mercury.

It is, however, always better, when possible, not to extract troilite from the iron, but from the cylindroid nodules in which the substance has concentrated. In these, sulphuretted iron contains only some graphite and stony matter, which can be got rid of by the action of the magnet. There is no doubt that this troilite is one of the most characteristic principles of meteoric iron. Notwithstanding this, its crystalline form has not yet been recognised, and there is some doubt about its chemical composition. The first chemists who examined it considered it as a variety of Breithaupt's pyrrhotine, and gave to it the formula Fe_7S_8 . But Professor Lawrence Smith concluded from his estimations of the sulphur in the iron of Tazewell, that it had the composition of a protosulphide, FeS . Notwithstanding this, he continued to give it the name of pyrrhotine, and thus a great confusion was introduced into science. Moreover, Professor Smith rested both upon the results of his own experiments and upon those obtained by several chemists in the examination of other samples of troilite; his conclusion was not admitted, and the existence of true crystalline magnetic pyrites in meteorites will increase the difficulties. The distinction between the troilite (or Professor Smith's pyrrhotine) and Breithaupt's pyrrhotine, is not so clear as would appear at first sight. The difference of composition is very slight, and the physical properties are very similar.

M. Meunier has lately had occasion to analyse several specimens of troilite taken from the meteoric irons of Charcas and of Toluca (Mexico), and the numbers which he has obtained have given him reason to think that the mineral in question is nearer to magnetic pyrites than to iron protosulphide.

Before giving the results of these analyses, we may call attention to a reaction which seems calculated to permit in all cases of the distinguishing of the iron protosulphide from magnetic pyrites, and, *a fortiori*, from compounds which are still richer in sulphur. When iron protosulphide is placed in a solution of copper, it precipitates this metal almost like iron itself; pyrrhotine, on the contrary, produces no such precipitation. The protosulphide obtained by the action of ammonium sulphide upon iron salts produces the same effect as the sulphide of exactly the same composition prepared by igneous means. This being well established, several samples of troilite were put into a solution of copper, and no precipitation could be observed; troilite, therefore, is very like magnetic pyrites in this respect, and we may draw the same conclusion as to its chemical composition. In fact, Professor Smith has based the formula FeS upon his analysis of Tazewell's troilite, which gave him:—

Iron	62.88
Nickel	0.62
Copper	trace
Lime	0.08
Silica	0.56
Sulphur	35.67
	<hr/>
	99.31

But these numbers show that the substance employed in his experiments was very impure.

Troilite purified by the process described above yielded a substance of which the specific gravity was 4.799. Its colour was bronze, and, its analysis gave:—

Iron	59.01
Nickel	0.14
Copper	trace
Sulphur	40.03
	<hr/>
	99.18

The formula Fe_7S_8 requires—

Iron	60.4
Sulphur	39.6
	<hr/>
	100.0

The Charcas troilite, previously purified, yielded—

Iron	56.29
Nickel	3.10
Sulphur	39.21
	<hr/>
	98.60

Its density is 4.78. The normal presence of nickel makes troilite a

species distinct from pyrrhotine, and its true formula becomes $(\text{FeNi})_7\text{S}_8$.

IV. **Schreibersite**.—Schreibersite, or iron and nickel phosphide, may be prepared by the same method as troilite. It is, besides, always preferable to select the schreibersite in the places where it is naturally concentrated. It is a yellowish, or almost white, metallic-looking substance. Its specific gravity is 7.108, and contains—

Iron	57.11
Nickel	28.35
Cobalt	trace
Magnesium	trace
Phosphorus	15.01
	<hr/>
	100.47

numbers which lead to the formula $\text{Fe}_4\text{Ni}_3\text{P}$. Schreibersite is magnetic, and takes permanent polarity by contact with a magnet. It is brittle. Hydrochloric acid has no action upon it. Its crystalline form has not yet been observed.

V. **Graphite**.—Graphite may be isolated by the following method:—A few grammes of metallic powder are projected into fused potash, and thus a mixture of nickeliferous iron and graphite is obtained. This mixture may be treated in several ways.

1st. The iron is dissolved in hydrochloric acid, which leaves the almost pure graphite as residue.

2nd. The graphite is separated by lixiviation. This process presents the advantage of giving both graphite and nickeliferous iron; but the separation is never complete.

3rd. When the graphite is abundant the magnet may be employed; in other cases it is drawn up with the metal.

In all cases the residue is washed by hydrochloric acid to dissolve foreign matters, such as troilite and schreibersite, or what is left after attacking with fused alkali.

The graphite extracted from the Caille iron has a specific gravity of 1.715. Its analysis gave—

Carbon	97.3
Iron	2.4
Nickel	trace
	<hr/>
	99.7

The graphite of the Charcas iron has a density of 1.809, and yielded on analysis—

Carbon	98.0
Iron	0.9
	<hr/>
	98.9

The graphite is remarkable on account of its great unalterability.

VI. External Crust.—Those portions of meteoric iron upon which is a crust, being separated by means of a saw, they are placed in a concentrated solution of mercury bichloride. After a sufficient time all metallic particles are dissolved, and the oxides, amongst which is the crust, remain alone.

The crust is, however, still mixed with foreign matters. It usually contains with it the products of its alteration by atmospheric agents, and particularly limonite. Some schreibersite, troilite, and stony grains may also be mixed with the principal substance, and their separation is very difficult. Weak hydrochloric acid carries away limonite and troilite; earthy particles remain as residue after the action of the magnet; lixiviation permits of the purification of the crust from schreibersite. These operations may, however, be simplified by choosing those portions of the crust that seem almost pure. They frequently detach themselves from the subjacent metallic matter.

Very few chemists have analysed the external crust of meteoric irons. The analyses given by Pugh, as showing the composition of the crust of the Toluca iron, were evidently executed on an impure portion. These are Pugh's results:—

Metallic iron	18.717
Iron protoxide	19.309
Iron sesquioxide	32.750
Nickel and cobalt protoxides	5.751
Chalk	trace
Silicates	10.203
Water	13.270
Chlorine	trace
	<hr/>
	100.000

The metallic iron, silicates, and water are evidently not essential elements of the crust, and must be considered as impurities.

Having purified as much as possible by the method above described the crust of the Toluca meteoric iron, M. Meunier found it possessed a density of 4.89, and the following composition:—

Iron sesquioxide	68.93
Iron protoxide	28.12
Nickel protoxide	2.00
Cobalt protoxide	trace
	<hr/>
	99.05

These numbers agree with the formula $\text{Fe}_2\text{O}_3, (\text{FeNi})\text{O}$, which does not differ from that of magnetite, except by the substitution of a small portion of nickel for a corresponding quantity of the iron of the protoxide. If in Pugh's analysis we only consider iron sesquioxide,

iron protoxide, and nickel and cobalt protoxide, we arrive at numbers very near to those required by the above formula.

VII. Stony Grains.—Several of the operations described above evidently yield the stony grains in a state of purity. But when it is especially intended to obtain these grains, they should be separated in the following way :—

The meteoric iron in the form of lumps is left protected from the contact of the air in a concentrated solution of mercury bichloride, and frequently stirred. After a sufficient time, the metal disappears, and the liquid contains the stony particles mixed with mercury protochloride, and generally with a small quantity of metallic mercury, besides troilite, schreibersite, and graphite. A solution of chlorine carries off the calomel, and the magnet removes the schreibersite and the troilite; lixiviation may be employed to get rid of graphite.

These grains are of different composition, and it appears that there exists a certain relation between their composition and their situation. Some are localised in the iron; others are situated in the troilite, or perhaps, in the graphite which surrounds this sulphide.

The grains of the first category may be found in meteoric irons of Tazewell and of Tucson. They consist of peridotite, and this is confirmed by the analyses published by Mr. Lawrence Smith. Their density is equal to 8.85.

The grains of the second category are yielded by the troilite of the Caille iron. Submitted to blowpipe assay, they only exhibit the reaction of silica.

The troilite of Charcas iron gave analogous results.

VIII. Gases.—Gases have been recognised in the meteoric iron of Lenarto, by Mr. Graham and by M. Boussingault.

M. Meunier has sought for the same bodies in another iron of the same origin by effecting the solution of those masses in concentrated mercury bichloride. As, however, he was not aware that the occluded hydrogen would be all absorbed by the solution of mercury bichloride, reducing it to the state of calomel or metal, he erroneously considered that the absence of visible gas proved that there was no gas occluded. The mass of Krasnojarsk (Siberia) gave a small bubble of gas, having the composition of atmospheric air; but it must be remarked that this iron was cracked.

IX. Rare Substances.—In concluding this enumeration, chromite and iron protochloride must be mentioned as having been found in certain irons. Their separation is evidently easy, and their composition is identical with that of analogous terrestrial compounds.

After having described the methods which have permitted him to separate in a state of complete purity the *immediate principles* of meteoric irons, M. Meunier remarks that these methods can be employed to estimate the relative quantity of the substances in question.

He has, for instance, submitted to a *quantitative immediate analysis*

the meteoric iron discovered in 1784, at Xiquipilco, in the valley of Toluca (Mexico), and has found in it—

Nickeliferous iron	96.301
Graphite	1.176
Troilite	1.482
Schreibersite	1.232

100.191

Special Methods for the Analysis of Iron Ores.¹

Three principal methods of analysis may be employed, which, in the subsequent descriptions, will be denoted as Method No. I., Method No. II., or Method No. III., according as one or other was employed in the particular analysis.

Details of Method No. I.—1. A portion weighed from the stoppered bottle containing the fine powder was digested in strong hydrochloric acid till no further action seemed to take place, and was boiled for about 15 minutes before dilution and filtration. The undissolved portion was thoroughly washed with hot distilled water, dried, ignited and weighed, the usual precautions being taken to prevent absorption of moisture.

2. The iron in the filtrate was peroxidised, if necessary, by nitric acid or potassium chlorate; excess of ammonia was added, and filtration conducted rapidly.

3. The calcium was precipitated from the filtrate as oxalate, converted into carbonate by ignition, and either weighed as such after evaporation with ammonium carbonate, or else moistened with sulphuric acid, and, after expulsion of the excess of acid by heat, weighed as sulphate.

4. The magnesium was precipitated by sodium phosphate and excess of ammonia. Generally, about twenty-four hours were allowed for the separation of the precipitate; it was then collected on a filter, washed with ammonia water, dried, ignited, moistened with a few drops of nitric acid, re-ignited, and weighed. The precipitate obtained by this method generally contains some flocculent matter, which was found to be aluminium phosphate, the alumina having been retained in solution by the ammonia (2).

5. The precipitate (2), consisting of all the iron, aluminium, phosphoric acid, and manganese (except a trace of the last which accompanies the lime), together with small portions of silica and lime or magnesia—the former combined apparently with alumina, the latter with a portion of the phosphoric acid—was dissolved in hydrochloric acid, then supersaturated with caustic potash, boiled in a platinum

¹ These methods were, after numerous experiments, finally adopted by Messrs. A. Dick and J. Spiller, in the analyses of the iron ores of Great Britain. (*Memoirs of the Geological Survey of Great Britain.*) The Iron Ores of Great Britain. Part I.: The Iron Ores of the North and North-Midland Counties of England.

basin, and filtered. The filtrate was acidified with hydrochloric acid, boiled, after addition of some potassium chlorate, to destroy the organic matter arising from the action of the potash on the filter, nearly neutralised with ammonia, and finally rendered alkaline with ammonium carbonate. The precipitate was ignited and weighed; the phosphoric acid contained in it was determined by the tartaric acid process (see par. 13, p. 208), and subtracted from the previous weight to ascertain that of the alumina. The amount of phosphoric acid so determined is never exactly the correct one, owing chiefly to its containing a little aluminium silicate. The phosphoric acid was always determined by another experiment.

6. The precipitate produced by caustic potash was dissolved in hydrochloric acid, and the iron precipitated as succinate, collected on a filter, redissolved and reprecipitated by ammonia, ignited, and weighed. So obtained, it is never perfectly pure, owing to its containing a little phosphoric acid, combined apparently with calcium or magnesium, and silica combined apparently with aluminium; neither of these combinations being decomposed by boiling with caustic potash. It was accordingly redissolved in hydrochloric acid, and filtered from a portion of the silica which becomes insoluble at this stage, and which was ignited and weighed. It may be here noted that a very small quantity of silica cannot be separated from a very large quantity of iron by the ordinary evaporation process; so that the separation of this small quantity of silica could not be effected by evaporation of the original hydrochloric acid solution. The phosphoric acid contained in the precipitate was determined by the tartaric acid process; so obtained, it generally contains a small quantity of aluminium silicate. This phosphoric acid and silica subtracted from the original weight gave what was taken as iron peroxide; though it no doubt still contained a very small quantity of other substances.

7. The filtrate from the iron succinate was rendered alkaline by ammonia; a few drops of bromine were added, and it was left twenty-four hours. The precipitate was ignited at a bright red heat and weighed as manganoso-manganic oxide.

8. The insoluble portion (1) was fused with excess of the alkaline mixture obtained by decomposing Rochelle salt by heat and washing out the mixed carbonates. The fused mass was dissolved in dilute hydrochloric acid, evaporated to dryness, the residue moistened with strong hydrochloric acid, and left twenty-four hours; it was then digested with hot water, filtered, and the silica ignited and weighed. Its purity was tested by dividing it into two portions, and treating one by hydrofluoric acid and the other by caustic potash; any impurity was separated if the amount was weighable.

9. The filtrate (8) was rendered alkaline by ammonia, and filtered. The precipitate was either ignited and weighed, the iron being afterwards separated and subtracted from the previous weight, or else it was at once dissolved in hydrochloric acid, and subjected to the potash

treatment described in (5) and (6), except that, since it contained no phosphoric acid, this part of the treatment was not needed.

10. The calcium and magnesium in the filtrate (9) were determined in precisely the same manner as in the hydrochloric acid solution of the ore.

11. *Alkalies and Organic Matter*.—It was ascertained that nearly the whole of the alkalies was contained in the residue insoluble in hydrochloric acid. A weighed portion of the ore was digested in hydrochloric acid, the insoluble residue collected on a filter, and washed. The latter was then dried, till, by a little management, it could be collected together and removed from the filter without detaching a weighable amount of the fibre of the paper. It was then exposed in a platinum vessel to the vapour of hydrofluoric acid in Brunner's apparatus till decomposed. The product was evaporated with strong hydrochloric acid, the residue moistened with dilute hydrochloric acid, and the undissolved black matter collected on a small weighed filter, dried, and weighed. As it generally contained a small amount of undecomposed inorganic matter, it was ignited and the ash weighed and subtracted. The filtrate from the organic matter was added to the original hydrochloric acid solution; the mixed solution was treated by the ordinary caustic baryta process for alkalies, which were weighed as chlorides.

12. *Sulphuric Acid and Sulphur*.—A weighed portion of the ore was digested in hydrochloric acid, the solution filtered, and the sulphuric acid precipitated from the filtrate as barium sulphate, ignited, and weighed. The residue was detached from the filter, mixed with potassium carbonate and nitrate, and fused in a gold crucible. The fused mass was dissolved in hydrochloric acid, evaporated to dryness, moistened with strong acid, diluted, and filtered. From the filtrate the sulphuric acid was precipitated as barium sulphate, and from this the sulphur was calculated. It seems always to have occurred as iron pyrites in the ore. In tabulating the results accordingly, the iron required to combine with this sulphur was subtracted from the percentage of insoluble residue, as well as from the composition of that residue. It may be here noted that when finely divided iron pyrites is boiled with strong hydrochloric acid and iron perchloride, some of the latter is reduced and some sulphuric acid formed. It is important to remember this in the analysis of hæmatites.

13. *Phosphoric Acid*.—A weighed portion of the ore was digested in hydrochloric acid, and the solution filtered. The filtrate was heated (the iron reduced by sodium sulphite when necessary), nearly neutralised with sodium carbonate, and excess of sodium acetate added. The liquid was boiled, and iron perchloride added, drop by drop, to the hot solution, till the precipitate had a decidedly red colour. The precipitate was collected on a filter, washed with hot water, dissolved in hydrochloric acid, tartaric acid added, and, finally, excess of ammonia.

The phosphoric acid was precipitated by addition of the mixture of magnesium sulphate, ammonium chloride, and free ammonia, 24 hours being allowed for the precipitate to separate. It was then collected on a filter, dissolved in hydrochloric acid, and some tartaric acid added to the solution. The phosphate was reprecipitated by ammonia, collected on a filter, ignited, moistened with a few drops of nitric acid, re-ignited, and weighed.

14. *Water*.—A portion of the ore was weighed out, dried in the water-oven, and re-weighed to determine hygroscopic water. It was transferred to a tube closed at one end; the other end was then connected by a cork to a small weighed tube containing calcium chloride. Heat was applied to the tube containing the powder, and gradually increased to low redness. The majority of the ores suffer decomposition during this, with evolution of a gas arising from the decomposition of carbonates, which prevents, in most cases, the necessity of drawing any air through the apparatus. The tube containing calcium chloride was then re-weighed to ascertain the amount of chemically combined water. In clay ironstones this is combined with the aluminium silicate or clay which they contain in admixture.

15. *Carbonic Acid*.—The single flask apparatus was used; sulphuric acid was employed to decompose the carbonates in the ore.

16. *Metals Precipitable by Sulphuretted Hydrogen from the Hydrochloric Acid Solution*.—A weighed portion of the ore, varying from 200 or 300 grains to 2000 grains, was digested for a long time in hydrochloric acid. The solution was filtered off (the iron in the filtrate reduced, when necessary, by sodium sulphite), and a current of sulphuretted hydrogen passed through it. A small quantity of sulphur which always separated was collected on a filter and thoroughly washed. It was incinerated at as low a temperature as possible. The residue was mixed with sodium carbonate, and heated upon charcoal before the blowpipe; and any globules of metal obtained were dissolved and tested.

Sometimes the portion insoluble in hydrochloric acid was re-digested in hydrochloric acid, and potassium chlorate added from time to time. The solution was then filtered off, and added to the original solution before reduction of iron per-salts.

Details of Method No. II.—A weighed portion of the ore was digested in hydrochloric acid, and the liquid filtered. The insoluble matter was fused as in Method No. I., dissolved in hydrochloric acid, and added to the original solution. The mixture was then evaporated to dryness to obtain the silica. In other respects the method of analysis was precisely similar to that described as No. I., avoiding only that part referring to the separate treatment of the matter insoluble in hydrochloric acid.

Details of Method No. III.—1. This method, owing to its greater simplicity and accuracy, was the one ultimately adopted. A

weighed portion of the ore was digested in hydrochloric acid, and the liquid filtered. The insoluble matter was ignited, weighed, and treated in a manner precisely similar to that described under Method No. I.

2. The iron in the hydrochloric acid solution was peroxidised when necessary. The solution was heated, nearly neutralised with ammonia, then boiled with excess of ammonium acetate, and filtered whilst hot. The precipitate was washed with hot water. The filtrate was received in a flask, and rendered alkaline by ammonia; a few drops of bromine were added, and the flask was tightly corked to exclude air, and left 24 hours. The liquid was then heated, and rapidly filtered; the precipitate was ignited, and weighed as manganoso-manganic oxide. The calcium and magnesium contained in the filtrate was determined as in Method No. I. It may be here noted that the magnesium ammonio-phosphate obtained by this process is never mixed with any aluminium phosphate, owing to the aluminium being completely precipitated as basic acetate.

3. The precipitated basic acetates (2) were dissolved in hydrochloric acid. The solution was supersaturated with caustic potash boiled in a platinum basin, and filtered. The aluminium containing some phosphoric acid was precipitated from the filtrate as in Method No. I. The phosphoric acid was separated by the tartaric acid process; the magnesium ammonio-phosphate was always redissolved and reprecipitated, but still was seldom quite pure, containing generally a little aluminium silicate. Another determination was always made. It was ascertained that when this method was employed no phosphoric acid remained with the iron after treatment with potash. A little silica, however, did remain, but the quantity was small, and as nothing further was done with the iron after treatment with potash, this was lost from the analysis, a more accurate method for the determination of the iron being employed.

4. *Iron*.—Two determinations were always made by Dr. Penny's very accurate volumetrical process. The burette employed was graduated to cubic millimetres. Pure zinc was used to reduce the iron before adding the standard solution. When the ore contained both iron oxides, precautions were taken to prevent the action of the air on the solution whilst the ore was dissolving.

5. All the other ingredients of the ore were determined in the manner described under Method No. I.

In all cases the actual weights of the substances obtained during the analysis were given, so that corrections may be made should the atomic weights at present in use be altered at any future time.

Experiments on the Determination of Iron Peroxide and Protoxide when they exist together in an Ore.—Extremely unsatisfactory results having been obtained by the use of Fuchs's process, some experiments were made with weighed quantities of the

pure materials. The copper used was electrotype copper; the iron was in the state of peroxide prepared by precipitation and ignition. The hydrochloric acid was of known strength. The experiments were made in stoppered bottles filled with the liquid to exclude the air.

4.17 grains of iron peroxide were dissolved in twice the amount of acid required for complete solution, and poured into a stoppered bottle, containing a piece of sheet copper presenting about 8 square inches of surface. The stopper was tied down with caoutchouc, and the whole left at the ordinary temperature till the solution became nearly colourless. About 16 days were required. The copper was then washed, first with a hot solution of common salt, and afterwards with pure water. It had lost 8.26 grains, whereas it ought to have lost 8.29 had the whole of the produced copper chloride been converted into dichloride. The bulk of the liquid was about $1\frac{1}{4}$ ounce. Similar experiments with twice and ten times the above amount of acid yielded like results; as also did an experiment in which 80 grains of sodium chloride were used instead of excess of acid to dissolve the dichloride as it formed.

Similar experiments were made at 100°C. , with like results, only that the change, which at the ordinary temperature takes many days, is effected in a few hours.

8.89 grains of iron peroxide, dissolved in twice the amount of acid requisite for solution, were treated exactly as above, except that the bottle was kept in a bath at 100°C. The solution became colourless in a few hours, and the copper was found to have lost 2.74 grains, whereas it ought to have lost 2.68. A similar experiment, in which five times the requisite amount of acid was employed, and another in which 20 grains of sodium chloride were employed, instead of excess of acid, also yielded results which were nearly accurate. It was found, however, that when this process was applied to the analysis of the ores it sometimes did not yield such accurate results.

Margueritte's volumetric method was used once or twice, but laid aside in favour of Dr. Penny's, owing to the trouble of preparing the solution, and keeping it of known strength. The solution of potassium bichromate employed was much weaker than that employed by Dr. Penny. To show the accuracy of this process, some of the experiments which were made for the purpose of testing it are given. They are quoted without selection, being just in the order in which they were made. The iron employed was fine iron wire. Quantity taken, 4.025; found, 4.050; taken, 2.90; found, 2.91; taken, 4.29; found, 4.285; taken, 6.51; found, 6.505; taken, 4.10; found, 4.07; taken, 5.85; found, 5.87; taken, 4.77; found, 4.77 grains. The mean error of the seven experiments was rather more than 0.01 grain of iron.

Fusing Iron Ores with Potassium Bisulphate.

On attempting to dissolve hæmatite and other iron ores in hydrochloric acid, a certain residue remains; and instead of having recourse to fusion with sodium carbonate to separate the silica and iron, fusion with potassium bisulphate at a dull red heat may be employed, which converts the iron into a sulphate, leaving the silica beautifully white. The time is, for 1 gramme of mineral, about 10 to 15 minutes.

Preservation of Proto-Salts of Iron.

Iron protosulphate may be preserved from oxidation by placing with it a piece of camphor wrapped in clean dry paper.

Iron protochloride may be obtained pure by evaporating the fresh solution almost to dryness, and adding powdered iron and strong hydrochloric acid in the proportion of one part of the former to five of the latter: the mixture is then evaporated to dryness with continued stirring by an iron spatula. The nascent hydrogen evolved effectually reduces all the sesqui- to the proto-chloride, and the dry salt will keep for a considerable time.

Separation of Iron from Aluminium.

Wöhler's process, which we have used with success for many years, is to neutralise the very dilute solution of these two bases with sodium carbonate, then add sodium thiosulphate, and, finally, heat till no more sulphurous acid is disengaged. In this manner all the alumina collects together into a precipitate, which may be calcined. The iron remains in the liquor, which should be concentrated and then decomposed with potassium chlorate and hydrochloric acid. After filtration to remove sulphur, precipitate the iron sesquioxide by ammonia.

Mr. Parnell describes a method very similar to the above, as being in use in some continental laboratories. To the slightly acid solution of the oxides a solution of sodium thiosulphate is added, more than equivalent to the amount of free acid present. The liquid is then boiled in a flask for about 10 minutes or a quarter of an hour. The whole of the alumina will be thrown down in a fine granular state, together with the sulphur resulting from the decomposition of the thiosulphuric acid; while the whole of the iron will remain in solution. The liquid is then rapidly filtered, and the precipitate washed with boiling water, dried, ignited in a porcelain crucible, and weighed in the usual manner. The filtrate containing the iron is treated with sodium hypochlorite, nitric acid, or other oxidising agent, and the iron estimated by precipitation by ammonia and weighing as sesquioxide. Care should be taken to avoid large excess of acid in the first instance, and also, subsequently, of the thiosulphate; the smaller the proportion of sulphur with the precipitated alumina, the more easily may it be filtered off from the iron solution. After calcination, the alumina

appears as a perfectly white crystalline powder, much resembling precipitated and calcined silica.

The method of weighing the two oxides together, and then separating the alumina by fusion with caustic soda and subsequent treatment with water, is accurate but troublesome. The plan of effecting the separation of the iron by means of ammonium sulphide from the ammonio-citrate solution of the oxides does not give perfectly accurate results, since the ammonium sulphide has the power of holding up small quantities of iron in solution; this may be proved by letting the perfectly clear filtrate stand a few days, when small flakes of iron sulphide will be deposited.

Another excellent plan to separate iron and aluminium is to put the calcined precipitate of the two oxides in a porcelain boat, and introduce it into a tube of the same material, heat to bright redness, and pass a current of dry hydrogen, which is kept up whilst the tube is cooling. The hydrogen is then replaced by a current of gaseous hydrochloric acid, and the tube being reheated, the iron, reduced by the hydrogen, is converted into a volatile chloride, whilst the alumina is left behind and may be weighed. (See the chapter on Silicates.)

Mr. F. M. Lyte effects the separation of alumina from iron by means of a boiling solution of baryta-water. The iron sesquioxide may be dissolved in sulphuric acid, reduced with zinc, and titrated by permanganate or bichromate, and the barium having been extracted by similar means from the filtrate, the precipitated barium sulphate is to be separated by decantation and washing, when, in the liquid thence obtained, the aluminium hydrate is precipitated by ammonia with the usual precautions. The estimation of the iron, if performed volumetrically, is scarcely, if at all, interfered with by the presence of barium sulphate, so that it is scarcely worth while to separate the latter before titration.

Mr. R. W. Emerson Macivor gives the following indirect process:—The aluminium and ferric hydrates are thrown down from solution in the ordinary manner, by the addition of ammonium hydrate, and the precipitate is collected on a filter, dried, ignited, and weighed. The ignited precipitate is then rubbed to a fine powder in an agate mortar, and carefully washed into a long-necked flask. Metallic zinc (quite free from iron) is next added to the contents of the flask, and finally some sulphuric acid. The whole is then heated over an Argand burner until the oxides have dissolved. The quantity of iron in the fluid is then estimated volumetrically by the potassium permanganate process. From the iron found, the quantity of ferric oxide contained in the precipitate is calculated, and this amount subtracted from the total weight of the mixed oxides gives, of course, the quantity of alumina contained in the mixture.

M. Ad. Carnot proposes the following method:—The two oxides

being dissolved in nitric or hydrochloric acid, there is added pure tartaric acid (about 1 gramme) or potassium bitartrate, and then ammonia in such a quantity that the liquid may become very clear. Ammonium sulphide is then added, the liquid is stirred, and the iron sulphide when deposited is poured upon a filter and washed. The separation is perfectly distinct, provided that the precipitate is not so bulky as to retain by adherence an appreciable proportion of alumina. The iron may then be estimated either gravimetrically or volumetrically. In order to estimate the alumina there is added, according to its presumed proportion, a quantity of sodium hydrate more than sufficient. The sulphuretted liquid is then decomposed by hydrochloric acid in slight excess (1 c.c. above the quantity needed for exact saturation), 4 to 5 grammes sodium acetate are then added, and the liquid is raised to a boil. It is kept near 100° for one to two hours, allowing the liquid to become concentrated. The mixture is then poured upon a filter, and washed for a few moments with boiling water.

To remove the tartaric acid with which the precipitate is impregnated, it is redissolved in nitric acid, diluted with water, almost neutralised with ammonia, a few drops of phosphoric acid and 2 to 3 grammes ammonium acetate added, and the mixture is boiled for an hour.

The precipitate formed is gelatinous, but there is so little fixed saline matter in the precipitate that after a short washing with boiling water no sensible traces remain in the precipitate. It may be incinerated without detaching from the filter. The phosphate is white, pulverulent, readily soluble in cold dilute nitric acid, and contains 42.04 per cent. of alumina.

The precipitation should be effected in liquids not very dilute, and the washing should be effected with a little boiling water, so as to render the loss as slight as possible, for the phosphate is not perfectly insoluble. But 100 c.c. of boiling water dissolve in reality less than 0.001 gramme of the compound.

The precipitation may even be effected in a complete manner by means of tartaric acid alone, without the addition of an alkaline acetate; but in this case it is more difficult to wash.

In order to separate alumina as phosphate from chromic oxide, the latter must first be transformed into chromic acid by fusion with pure potash and nitre. It is then dissolved, and the liquid is acidified slightly with nitric acid. A little sodium phosphate and 4 to 5 grammes sodium acetate are then added, and the liquid raised to a boil. The aluminium phosphate is precipitated alone. It is washed with a little boiling water in order to remove all the chromic acid, redissolved in nitric acid, and the estimation of the alumina is completed as above. The filtrate is raised to a boil, and there is gradually poured into it aluminium nitrate enough to throw down all the phosphoric acid. It is boiled for half an hour and filtered. The

filtrate when cold is mixed with lead acetate, when the chromic acid is precipitated and weighed as lead chromate.

Separation of Iron from Zinc.

If the presence of barium is not objectionable, add barium carbonate to the nearly neutral solution of zinc and iron sesquioxide. The whole of the iron sesquioxide will be precipitated, leaving all the zinc in solution. Or, the solution may be nearly neutralised with sodium carbonate, and after sodium acetate is added in excess, brisk ebullition will bring down all the iron as basic acetate. From the filtrate, acidified with acetic acid, a stream of sulphuretted hydrogen will precipitate the zinc.

Separation of Iron from Uranium.

When, as is generally the case, ammonium carbonate is employed for this separation, it is well known that some of the iron is always dissolved with the uranium. The following is, however, a method for rendering the separation complete :—As uranium oxide in solution in ammonium carbonate is not precipitated by ammonium sulphide, add to the liquid, separated by filtration from the bulk of the iron oxide, a few drops of ammonium sulphide to eliminate from it, in the state of sulphide, the small quantity of iron which has been dissolved. After filtering again, a solution is obtained containing all the uranium without any trace of iron.

Separation of Iron from Chromium.

When the iron is in very large excess, the following is a good method for separating the chromium :—Treat the metal or ore by the ordinary processes, to separate the silica, and obtain a liquid containing all the metals in solution, and in which the iron is at its maximum of oxidation ; then precipitate the liquid by an excess of a strong solution of potash ; and pour, drop by drop, into the solution containing the precipitate (and heated to 80° or 90°), a dilute solution of potassium permanganate until the permanganate loses its colour ; the reaction is terminated when the liquid takes a greenish tinge, owing to the presence of potassium manganate. Then filter, and saturate the filtered liquid with acetic acid, which immediately reduces the small quantity of potassium manganate that gave to the solution its green colour. Into the liquid, which frequently has a yellow tinge, pour lead acetate, which determines a yellow precipitate of lead chromate, if the least trace of chromium be present.

Another method is to nearly neutralise the solution, containing chromium and iron peroxide, with sodium carbonate, and add sodium acetate in excess. A current of chlorine gas or addition of chlorine water then readily converts the whole of the chromium present into chromic acid. Upon now boiling the solution, the excess of chlorine

is expelled, whilst, at the same time, the iron is precipitated as basic acetate. The chromic acid in the filtrate may either be reduced with alcohol and hydrochloric acid, and the chromium sesquioxide precipitated with ammonia, or lead acetate may be added and the lead chromate collected.

If it is not desired to precipitate the iron as basic acetate it may be precipitated with ammonia; all the chromium will remain in solution as chromic acid.

Estimation of Chromium in Iron and Steel.

Mr. J. O. Arnold proceeds as follows: Weigh out from 1 to 5 grammes of the steel (in drillings), according to the amount of chromium present (this may be ascertained by a rough colorimetric test). Place the metal in a wide, covered beaker, and add 20 c.c. of strong hydrochloric acid; heat till all action is at an end, rinse the cover and sides of the beaker from splashing, and evaporate the solution *gently* to complete dryness. If the evaporation has not been too rapid, the chlorides may be almost entirely detached from the bottom of the beaker in a brittle cake. This is broken up into small pieces by means of a platinum spatula, and as much as possible is brushed out into a clean dry porcelain dish. A small quantity of the chlorides will, however, remain adhering to the beaker; this may be removed with 2 or 3 c.c. of dilute hydrochloric acid. The solution is poured into a deep platinum crucible, the beaker rinsed with 1 or 2 c.c. of water, the washings added to the crucible, the contents of which are now evaporated to dryness on a sand-bath. When dry the main quantity of the chlorides is carefully brushed out of the porcelain into the platinum dish, and is reduced to a fine powder by means of a little pestle made from a glass rod. The spatula and pestle are cleaned into the crucible. The finely-divided chlorides are now thoroughly mixed with an excess of fusion mixture (1 part dry sodium carbonate to 1 part powdered nitre), a cover is placed over the crucible, and its contents are fused over a gas blowpipe till quite liquid. By this treatment the iron is converted into insoluble oxide, the manganese, silicium, and chromium, respectively, into an alkaline manganate, silicate, and chromate. When cool the crucible is placed in a beaker containing 80 c.c. of boiling water, and is gently boiled till the fused mass is detached and dissolved out. This may be assisted by occasional stirring with a glass rod. When clear from oxide, remove the crucible and cover, washing them well with hot water. Add 8 or 4 drops of alcohol to decompose the manganate, and allow the iron and manganese oxides to settle thoroughly. When the supernatant liquid is quite clear it is decanted on a close double filter, the filtrate being received into a clean beaker. The precipitates are disturbed as little as possible. When all the clear liquid has passed through, the filter is well washed with hot water. The precipitates are now washed twice by decantation with 30 c.c. of

hot water ; at the second washing the contents of the beaker are allowed to drain *gently* into the filter, which is now allowed to drain thoroughly and is removed without further washing. These precautions in washing must be strictly carried out, as the ferric oxide is in such an exceedingly fine state of division that any attempt to wash or disturb it on the filter will inevitably cause some of it to pass through into the chromium solution. The *clear* yellow filtrate contains the chromium and silicium ; to it is added 20 c.c. of hydrochloric acid, the cover being kept on the beaker to prevent projection of the solution by the evolved carbonic acid. The solution is now well boiled until all the carbonic acid and nitrous fumes are driven off. Its colour will now be green, owing to reduction to chloride. Dilute ammonia is added to alkaline reaction, and the solution heated nearly to boiling. The resulting precipitate is collected on a filter (previously well washed with hot dilute hydrochloric acid to free it from iron), and is slightly washed. When the washings have drained through, the precipitate is dissolved off the filter with hot dilute hydrochloric acid, the filtrate being received into the beaker in which the precipitation took place. The solution is now evaporated to dryness to render the silica insoluble. The soluble chromium chloride is taken up with 10 c.c. hydrochloric acid and 90 c.c. of water, and is filtered through a washed filter into a clean beaker, the filter being well washed. The precipitation is now repeated as above, and the chromium hydroxide comes down free from silica and alkaline salts. It is collected, washed, dried, ignited, and weighed as chromic oxide. Only 3 or 4 drops of alcohol should be added, as this quantity is sufficient, not only to precipitate the manganese, but also to effect the reduction to chloride. If too much is added organic compounds are formed, which tend to prevent the complete precipitation of the hydrate. The ammonia in the last precipitation should be added in the least possible excess, and the solution should be heated gently *nearly* to boiling. If any great excess of ammonia be present, and if the solution is boiled, the glass of the beaker is attacked and the result is high. The method, if carefully carried out, is accurate.

Estimation of Chromium and Tungsten in Steel and in Iron Alloys.

Mr. R. Schöffel first removes the greater part of the iron by treating the comminuted material with the double copper and sodium or copper and ammonium chloride. The residue, which contains all the chromium, combined with small quantities of iron, in a porous state, is rendered soluble by fusion with saltpetre and sodium carbonate. The melted mass, which may be coloured green by manganese, is digested with water till the rest appears pulverulent, whereby any manganic acid is decomposed, and the liquid is filtered. A solution is thus obtained, containing the chromium as an alkaline chromate. If

no important proportion of silica is present, as in some kinds of cast steel, the liquid may be cautiously neutralised with nitric acid, precipitated with mercurous nitrate, and the chromium estimated in the well-known manner, but as notable quantities of silica may be present in the solution, especially in crude chrome irons, it must first be removed by the usual process. The solution of the melted mass is neutralised with hydrochloric acid, a small quantity of alcohol being added, and evaporated to dryness. After filtering off the silica, the chromium is precipitated with ammonia and ammonium sulphide in the usual manner.

This method is universally applicable for chrome steel, but for crude chromium and chrome-iron alloys it is available to a certain limit only. If such a compound contains more than about 8 per cent. of chromium, then on treatment with the double salt of copper a part of the iron is indeed dissolved, but the less the higher is the percentage of chromium. The residue does not assume that porosity which is required for the treatment with nitre and soda.

In such cases the only expedient is to digest the comminuted material for a long time in hydrochloric acid with the aid of heat. It is an erroneous supposition, that on treating such iron with hydrochloric acid the chromium is found in the residue. If the proportion of the chromium is low it is entirely dissolved, even in dilute acid. In richer alloys a portion of the chromium remains undissolved. If the chromium exceeds about 30 per cent., neither this metal nor the iron dissolves on prolonged digestion in hot acid. Such alloys are not attacked either by aqua regia, bromine, or cupric chloride.

The portion not dissolved in hydrochloric acid is fused in the usual manner with sodium carbonate and saltpetre, the melted mass is dissolved in water and hydrochloric acid, and the solution mixed with that already obtained by treating the iron with hydrochloric acid. The chromium is then estimated in this solution by a process devised by E. Donath.

The solution is neutralised so far that it still remains distinctly acid, and mixed with sodium acetate, which should occasion no precipitate. Solution of permanganate is then added, and the whole heated to a boil, when the greater part of the iron is precipitated. The supernatant liquid, after boiling, should still appear distinctly red. A few drops of alcohol are then added till the colour disappears; sodium carbonate is then added to complete the precipitation of the iron, the liquid is again heated and filtered. In the filtrate the chromium is found as alkaline chromate.

Or, instead of permanganate, the author adds bromine to an acid solution in presence of sodium acetate. If so much acetate is added that the liquid contains free acetic acid, but no hydrochloric acid, the oxidation takes place rapidly. The operation is best performed in a flask, which is closed after adding the bromine, and frequently shaken.

After some hours the bromine is expelled by boiling, and the iron completely precipitated with sodium carbonate. This method is especially recommended where a simultaneous estimation of manganese is required.

Estimation of Tungsten in Iron and Steel.

For the estimation of tungsten in steels and tungstiferous iron R. Schöffel employs the method given above for chromium. (See p. 217.) In the rare case of a notable proportion of silica, the tungstic acid, after being weighed, is melted with potassium bisulphate, the melt treated with water, and the undissolved silica deducted from the gross weight of the tungstic acid. If the tungsten exceeds 12 per cent., which rarely occurs, this method is open to the same objections as in the case of chromium, except the material is very finely pulverised. The residue, after treatment with the double copper salt, is washed, dried, and ignited in a crucible, with exposure to air before fusion with nitre and sodium carbonate.

M. Sergius Kern proceeds as follows in the estimation of tungsten and chrome in iron and steel:—

‘Five grammes of the specimen are dissolved in aqua regia, and the solution is evaporated to dryness, and then dissolved in a mixture of 25 c.c. of water and 15 c.c. of hydrochloric acid. The resulting precipitate contains silica and tungstic trioxide; it is next filtered from the solution, washed first by water acidulated by 5 per cent. of hydrochloric acid, and finally by pure alcohol. The tungstic trioxide is dissolved on the filter in strong ammonia; the filtrate is boiled for 20 minutes with 5 grammes of caustic lime or caustic potash; hydrochloric acid is next added, the solution is heated for some time, and the remaining precipitate of pure tungstic trioxide is filtered from the liquor, dried on the filter, carefully ignited, and weighed. It contains 79·81 per cent. of tungsten.’

In analysing chrome-iron alloys the following process may be used. The work is quickly executed:—From the solution containing iron and chromium, these metals are precipitated by ammonium sulphide; the resulting precipitate is filtered from the liquor, dried, and ignited for 30 or 40 minutes in a platinum crucible, with four parts of a mixture of equal quantities of nitre and potassium carbonate. The ignited and fused mass is placed in a glass, and hot water with 5 per cent. of alcohol is next added. The liquor is boiled and filtered from the precipitate; the solution contains only the chromium salt, which is precipitated in the form of chromium hydrate by adding an excess of ammonia; this is strongly ignited; the resulting chromium oxide is weighed and the percentage is calculated, knowing that this compound contains 82·2 per cent. of chromium. In analysing iron and steel the manganese is usually separated from the iron by sodium acetate, which throws down the iron and leaves the manganese in solution. The man-

Handwritten note:
 The Tungstic acid is dried in a crucible at 100°C. for 24 hours.

ganese is precipitated either by ammonium sulphide in the form of manganese sulphide, or by bromine in the form of hydrated manganese dioxide, which is next ignited, and the resulting manganese compound, manganoso-manganic oxide, is weighed. The first process of precipitation of manganese by ammonium sulphide is, however, a dirty operation, giving at the same time not such correct results as the bromine process. But as bromine is expensive, the use of it in laboratories is limited. The strong irritating smell is also a drawback in using this element for analytical researches. S. Kern proposes to replace the bromine in this case by sodium hypochlorite, which, in solutions of manganous salts in the presence of an alkali, throws down the manganese in the form of hydrated manganese dioxide.

Valuation of Chrome-Iron Ores.

Half a gramme of the finely pulverised ore is taken and fused in a platinum crucible with three times its weight of potassium bisulphate for one hour; then allowed to cool, and the same amount of a mixture of equal parts of potassium nitrate and sodium carbonate put on the top, and again fused for another hour, allowed to cool, and digested in a porcelain dish for two or three hours with water on the sand-bath, then filtered and well washed out with boiling water. The filter is treated with hydrochloric acid for two or three hours in a warm place until the iron sesquioxide is dissolved; filter again, and if there is not too much undecomposed ore remaining, it can be weighed and deducted, or if too much remains it must be again fused as before. The chromic acid solution is warmed, and ammonium carbonate added to precipitate any silica, aluminium, or calcium in solution; it is allowed to stand an hour and filtered; hydrochloric acid is then added to the solution until it is acid; it is next warmed, and sulphurous acid is added to reduce the chromic acid to sesquioxide; ammonia is then added, and the whole is allowed to stand twelve hours, after which it is filtered, the chromium sesquioxide washed by decantation, dried, ignited, and weighed.

M. R. Kayser proposes to attack this ore with a mixture of 2 parts of sodium carbonate and 1 part pure hydrate of lime. The mixture is maintained for half an hour at bright redness in an open crucible, with frequent stirring. The chromate formed may be easily extracted in boiling water.

Dr. Gent, of Philadelphia, who has had much experience in the analysis of chrome-iron ore, gives the following process. It is very trustworthy, although long and somewhat tedious.

Of the chrome ore, reduced to an impalpable powder, put 0.5 gramme in a platinum crucible about 2 inches high, nearly $1\frac{1}{2}$ inch wide, and holding 52 grammes of water, and place upon it 6 grammes of pure fused potassium bisulphate, and heat with the greatest care for about 15 minutes, at a temperature scarcely above the fusing-point of the

bisulphate; then the heat is gradually raised, but not higher than to make the bottom of the crucible red-hot, and kept at this temperature from 15 to 20 minutes. Never permit the mass to rise to half the height of the crucible. (If the fusion with potassium bisulphate is done too rapidly, a portion of the analysis is very apt to be lost by spirting, from the escape of sulphurous acid, resulting from the oxidation of the ferrous oxide by the sulphuric acid.) The mass begins now to fuse quietly, and vapours of sulphuric acid go off more freely; it should then be kept at a red heat for about 20 minutes, and the heat next raised as high as necessary to drive off the second equivalent of sulphuric acid, and even to decompose a portion of the sulphates of ferric and chromic oxides. To the fused mass add about 8 grammes of pure sodium carbonate, and fuse the mixture, and then, by degrees, keeping the temperature for about 1 hour at dull red heat, about the same quantity of saltpetre; next heat for 15 minutes at a bright red heat. The fused mass is dissolved in boiling water, filtered whilst boiling, and washed with boiling water.

The insoluble residue, containing the greater portion of the silicic acid, titanitic acid, alumina, iron sesquioxide, zirconia, and—if the fusion has been conducted at a temperature sufficiently high to convert the saltpetre into caustic potash, and the above precautions have been used—all the magnesia, is redissolved in dilute warm hydrochloric acid, which generally dissolves it readily and completely, and rarely leaves undecomposed ore behind; but if so, this residue must invariably be fused in a small crucible as before, adding, after the separation of the insoluble portion, the solution containing the small quantity of chromic acid to the first filtrate. (The certainly less troublesome method, to deduct the insoluble portion from the original weight, is bad; such residues have never the composition of the original ore.) The filtrate contains the whole quantity of the chromium as chromic acid, sometimes a trace of manganic acid, small quantities of silicic acid, alumina, and rarely titanitic acid. To this solution add an excess of ammonium nitrate, and evaporate over a water-bath nearly to dryness, and until all the liberated ammonia has been expelled. The precipitate remaining on addition of water contains the silicic acid, titanitic acid, alumina, and manganic oxide, which had gone into solution with the chromic acid; it is filtered off, and the filtrate made strongly acid with sulphurous acid, carefully heated to boiling, precipitated with a slight excess of ammonia, boiled for a few minutes and filtered. Dr. Genth says he formerly acidulated the chromic acid solution by hydrochloric acid, and then added sulphurous acid, but he several times observed that, although an excess of sulphurous acid had been used, a small portion of the chromic acid escaped reduction, the filtrate from the ammonia precipitate being yellow. He has in vain tried to find the reason for this singular behaviour. Since using sulphurous acid only, he has never been troubled with anything similar.

It is exceedingly difficult to wash out the chromic oxide; it succeeds best in the following way:—After the precipitate has settled, the clear liquid is passed through the filter, then boiling water is added to the precipitate, and after settling, the supernatant liquid is filtered; the precipitate is then put on the filter, and washed twice or three times with boiling water; it is then washed back again into the dish and boiled with water, until the little lumps which clog together are completely broken up, and it is then filtered again, and this operation repeated until the wash-waters do not show the presence of any sulphates when tested with barium chloride. The precipitate is then dried and burned. No matter how well it may have been washed, it almost invariably contains minute quantities of alkalis, in the presence of which a little chromic oxide is converted into chromic acid. The ignited precipitate is therefore put into a dish, boiled with water, a few drops of sulphurous acid added, precipitated by ammonia, filtered, washed, dried, ignited, and weighed.

In this manner the chromic oxide is obtained quite pure, and repeated analyses of the same sample of ore never vary 0.25 per cent. of chromic acid.

Mr. P. C. Dubois has found that finely pulverised chrome-iron ore may be completely dissolved by fusing it at a red heat for 10 or 15 minutes over a blast lamp with 4 or 5 times its weight of potassium fluorhydrate. The fused mass has a clear green colour. By treating this with sulphuric acid until the whole of the fluorine is expelled, and then adding water, the chromium, iron, and aluminium are completely dissolved as sesqui-salts. The easiest method of separation is the following:—To the solution an excess of caustic soda is added, after which, without filtering, chlorine gas is to be passed through until the chromium sesquioxide is converted into chromic acid. The solution is then to be heated to expel excess of chlorine, nitric acid added in slight excess, and the iron sesquioxide and alumina precipitated by ammonia. To the filtrate acetic acid is to be added in small excess; after which the chromic and sulphuric acids may be precipitated together by lead acetate. The precipitate, after washing, is to be boiled with hydrochloric acid and alcohol, the lead separated as chloride, and the chromium determined in the usual manner as sesquioxide. This method gives a complete separation, even when magnesium and nickel are present in the ore.

Estimation of Chromium in Chrome Iron.

Mr. F. C. Phillips heats the finely powdered chrome iron in a closed glass tube with sulphuric acid of sp. gr. 1.84 to 250°—300° C.; eight c.c. of acid suffice for 0.5 gramme of the ore. If a solution of a chromic acid salt is mixed with sodium carbonate in excess and bromine water is then added drop by drop with constant stirring, the chromium dissolves as sodium chromate. In this manner chromium

is completely separated from zinc, manganese, iron, and aluminium. For the separation of aluminium the solution must be very dilute, and but a slight excess of sodium carbonate is used. Heat is not applied till after the addition of the bromine.

When an estimation of the chromium only is sought, the decomposition of chrome-iron ore, according to H. N. Morse and W. C. Day, can be best accomplished by fusing the material with potassium hydroxide in a wrought-iron crucible.

The method here described has, without exception, given satisfactory results. From 6 to 10 grammes of potassium hydroxide are placed in a wrought-iron crucible (having the form of the ordinary porcelain crucible and a capacity of about 100 c.c.) and gently heated until the evolution of steam ceases and the fused mass becomes tranquil. After cooling, the finely pulverised material, weighing not more than 0.5 gramme, is placed upon the potassium hydroxide and evenly distributed over the surface. A flame just sufficient to thoroughly fuse the alkali is applied to the uncovered crucible, and the contents, as long as they remain in a fluid condition, frequently stirred with a piece of iron wire, which is allowed to remain in the crucible. The decomposition progresses rapidly, and the potassium hydroxide, together with the soluble products of the decomposition, soon begins to rise upon the sides of the crucible, where it deposits itself in forms somewhat resembling cauliflowers. Within two or three hours the decomposition is complete, and the bottom of the crucible becomes dry. The crucible is then turned upon its side and the temperature of its under surface raised to a dull-red heat. The incrustation on the interior of the crucible does not fuse at this temperature, but becomes rapidly yellow, owing to the oxidation of the chromium to chromate. At the end of two or three hours the oxidation is perfect. Portions of the incrustation retain a greenish colour, however long the heating is continued; but this is due to the presence of iron or manganese and not to unoxidised chromium.

After cooling, the crucible is placed in a porcelain evaporating-dish, and the contents removed by means of hot water. The solution, which at first has a greenish appearance owing to the presence of iron dissolved in the caustic potash, is heated for some time in order to effect complete precipitation of the iron. The filtrate, which has a clear yellow colour, is rendered slightly acid with a pure dilute nitric acid, the aluminium precipitating with ammonia and washed by decantation. The potassium chromate is then reduced, and the silica rendered insoluble by evaporating to perfect dryness with an excess of hydrochloric acid. The residue is moistened with hydrochloric acid and treated with water.

It only remains to separate the chromium in the filtrate from magnesium, and to estimate it as chromic oxide. To do this it is preferable in each instance to first precipitate with barium carbonate.

According to Dr. J. Clark perfectly accurate results may be obtained by the following process, which is both simple and expeditious:—25 grains of the finely pulverised ore are intimately mixed with 5 parts of sodium hydrate and 8 parts of calcined magnesia, and the mixture is exposed in a platinum crucible, with the lid on, over a Bunsen flame for three-quarters of an hour. Oxidation at once takes place under the influence of the sodium hydrate and magnesia, and it is practically complete in less than an hour. The crucible with its contents is then placed in a basin containing water, the contents being washed out with water as far as possible, and the operation completed by using dilute sulphuric acid quite free from nitric acid. An additional quantity of dilute sulphuric acid is added, and then the whole is heated. Everything will dissolve, except, perhaps, a few flakes of silica. To the clear yellow solution is added a known quantity of double iron and ammonium sulphate of known strength, and more than sufficient for the reduction of the chromic acid. The excess of unoxidised iron is then estimated with a weak standard solution of potassium bichromate, and the amount of chromium oxide in the ore calculated from the quantity of iron oxidised. The results obtained seldom vary 0·2 per cent.

W. J. Sell recommends the following plan of effecting the decomposition of chrome-iron ore:—The ore is placed on the top of about ten times its weight of a mixture composed of one part of well-fused and powdered sodium bisulphate to two parts of sodium fluoride, and the whole is ignited for 15 minutes. An amount of sodium bisulphate is now added equal to that of the mixture taken, and when thoroughly fused a further addition of an equal quantity of bisulphate is made, the mass fused, and then rapidly cooled. The fused mass so obtained dissolves completely in boiling water acidified with sulphuric acid.

Volumetric Valuation of Chrome-Iron Ore.

The following method for quickly and accurately determining the amount of chromium and iron in chrome-iron ores is given by Mr. J. Blodget Britton:—Reduce the mineral to the finest state of division possible in an agate mortar. Weigh off 0·5 gramme and add to it 4 grammes of a flux, previously prepared, composed of one part potassium chlorate and three parts soda-lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright red heat for an hour and a half or more. The mass will not fuse, but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and turn the powder into a tall 4-ounce beaker and add about 18 c.c. of hot water, and boil for 2 or 3 minutes; when cold, add 15 c.c. of hydrochloric acid of common strength, and stir with a glass rod for a few minutes, till the solid matter, with the exception, probably, of a little silica in a flaky gelatinous state, becomes dissolved. Both the iron and chromium will then be in the states of

iron sesquioxide and of chromic acid. Pour the fluid into a white porcelain dish of about 20 ounces capacity, and dilute with washings of the beaker to about 8 ounces. Immediately after, also, pour cautiously into the dish 1 gramme of metallic iron of known purity, previously dissolved in dilute sulphuric acid and further diluted with cold water to about 5 ounces, to make up the volume in the dish to about 8 ounces.

Use for this purpose fresh borings from a piece of bar iron, containing less than 0.05 of foreign matter, dissolved in 18 c.c. of dilute sulphuric acid of 1 part acid and $8\frac{1}{2}$ parts water, in a tube 12 inches long and $\frac{1}{4}$ inch diameter, closed at the top with an india-rubber stopper perforated for a $\frac{1}{4}$ -inch tube, bent short round at right angles and extending horizontally about 8 or 4 inches, applying heat to expel atmospheric air and facilitate operations.

When the iron is dissolved, and having ascertained that the solution is free from sesquioxide, nearly fill the tube with *cold* water and cautiously pour the contents into the dish and add about two tubeful more of *cold* water to make up the solution to about 8 ounces, and then estimate, volumetrically, with a standard solution of potassium permanganate, the amount of iron protoxide remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidised to sesquioxide by the chromic acid. Every one part so oxidised will represent 0.82 of metallic chromium, or 0.4668 of sesquioxide, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be estimated, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder, as already directed, dissolve it in a tube of the kind described, by adding, first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of hydrochloric acid, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure sheet zinc cut in small strips, sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease, and the zinc has become quite dissolved; then nearly fill the tube with cold water, acidulated with $\frac{1}{10}$ of sulphuric acid, and pour the contents into the porcelain dish, and add cold water to make up the volume to about 8 ounces, and complete the operation with the standard permanganate solution.

The process, if conducted as directed, affords very accurate results; upon repeating the estimations there should be practically no variation. The whole time consumed need not exceed 8 hours to estimate both the chromium and the iron, if the two ignitions are proceeded with simultaneously. Fine iron wire may, in most cases, be used with greater convenience than borings. Mr. Britton, however, prefers the latter, and keeps in the laboratory for use a large piece of iron of the kind mentioned, from which, by the aid of a small foot-lathe, he

obtains in a moment or two clean unoxidised borings whenever they are needed, and thus has an unalterable standard always at hand.

For dissolving minerals and metals, tubes of the kind described, though sometimes of a larger size, are generally preferable to all other vessels, for many reasons—avoidance of loss of substance, convenience of rinsing, expulsion of air while digesting and boiling, carrying out of the laboratory all the evolved gases by means of the small bent tubes leading into a chamber connected with the main chimney, &c.

Chrome-iron ore can also be readily broken up by Professor Storer's plan of oxidising with potassium chlorate and nitric acid (page 101). The following experiment shows the value of this method, but no further trials have as yet been made to test its applicability to quantitative analysis. A small quantity of chrome-iron ore was ground to very fine powder, and treated, in a dish, with nitric acid and potassium chlorate, as before described. At the end of half an hour, that portion of the ore which still remained undissolved was washed with water, dried, fused with a mixture of sodium carbonate and potassium nitrate, and the fused mass boiled with water; the solution thus obtained gave no reaction for chromium when tested for that substance.

Analysis of Chrome Iron and Steel.

Mr. W. Galbraith dissolves 1 gramme of the chrome iron in dilute sulphuric acid (about 6 parts of water to 1 of acid). Sufficient potassium permanganate to oxidise all the iron is now added, and then about as much more, and the solution boiled until the colour of the permanganate is destroyed. Potassium permanganate crystals are used, and it is necessary to have an excess of permanganate, otherwise some of the chromium may escape oxidation, especially if there is much chromium. The black or dark brown precipitate, consisting probably of a mixture of manganese permanganate and oxide is now filtered, washed well with hot water, and to the filtrate, which should of course be of a bright yellow colour, is added a known weight of ferrous sulphate, or preferably ammonio-ferrous sulphate, and the excess of iron estimated with a standard solution of potassium bichromate.

This method gives very accurate results, and as it does not occupy much time (not more than half an hour) it leaves little to be desired.

Steels are estimated in precisely the same manner, with the exception that 2 or 3 grammes of the sample are taken instead of 1.

Separation of Iron from Chromium and Uranium.

According to M. A. Ditte, the separation of these oxides may be effected with great accuracy by operating in the manner proposed by

M. Sainte-Claire Deville for the separation of iron and alumina. The metals are brought to the state of sesqui-salts; all metals whose sulphides are insoluble in dilute acids are removed by known methods, and the ferric, chromic, and uranic oxides are then precipitated together by an excess of ammonia. Care must be taken to drive off by ebullition any free ammonia which might dissolve a little uranium. The oxides are well washed, calcined, placed in a porcelain tube, and heated to redness in a current of pure hydrogen. The ferric oxide becomes metallic iron, the uranic oxide is reduced to uranous oxide, while the chromic oxide remains unaltered. This mixture of iron, uranium and chromium oxides is weighed, returned to the tube, and submitted to the action of a current of gaseous hydrochloric acid at a red heat. The uranium and chromium oxides remain entirely unattacked by the acid, and their weight suffers no variation. As for the iron, it is entirely volatilised as ferrous chloride, and deposited in white crystals in a cooler part of the tube. After an hour or an hour and a half the tube is allowed to cool in a current of hydrogen, to drive out the hydrochloric acid, and the mixture of chromic oxide and uranous oxide is weighed and treated with pure nitric acid. The uranium protoxide, which remains in the form of a brown amorphous powder, is at once attacked, even in the cold, with evolution of nitrous fumes and formation of uranium nitrate. It is well, however, to heat for a few moments, in order to be certain that the chromic oxide retains no traces of uranium; the solution is then filtered off, and the residue calcined and weighed.

Separation of Iron from Zirconium.

Render the solution nearly neutral with sodium carbonate, and add excess of sodium thiosulphate. Boil the liquid for a short time and all the zirconia will be precipitated, with a little sulphur, but perfectly free from iron, which will all be in solution.

The solution containing zirconium and iron may also be boiled with nitric acid to peroxidise the iron, and then precipitated with excess of ammonia. The precipitate is then digested with excess of oxalic acid, which dissolves the whole of the iron together with a trace of zirconia, but leaves the greater part of the zirconia in the form of an insoluble oxalate.

Or, the mixed precipitate of iron sesquioxide and zirconia may be digested in ammonium sulphide until the whole of the iron is in the state of sulphide. Decant the supernatant liquid and digest the black precipitate in a dilute solution of sulphurous acid. This dissolves the iron sulphide and leaves the zirconia quite colourless.

The process given on page 94 for the preparation of pure zirconia, &c., may also be used to separate iron and zirconium.

Separation of Iron from Titanium.

When iron sesquioxide and titanac acid are together in dilute solution, they can be separated by ebullition with sodium thiosulphate, as in the case of iron and zirconium. The titanac acid precipitates whilst the iron remains in solution. Or, add ammonia in excess to the solution, digest the mixed precipitate of titanac acid and iron sesquioxide with ammonium sulphide, and then dissolve out the iron with sulphurous acid.

Other methods of separating iron and titanium may be found under the heading Titanium (page 98), or under the description of the method of analysing titaniferous iron ore (page 197), and estimation of titanium in iron and steel (page 191).

Volumetric Estimation of Iron and Titanium.

The amount of titanium and iron in a solution may be estimated volumetrically in the following manner:—Add metallic zinc to the slightly acid solution until the titanium is reduced to the state of violet sesquioxide and the iron to protoxide. Then decant from the zinc, and add from a burette a standard solution of potassium permanganate until the violet colour disappears, finding the moment at which the iron begins to oxidise in its turn by taking from time to time a drop of the liquid and mixing it with a drop of potassium sulphocyanide in a porcelain capsule. When the sulphocyanide begins to be coloured, the number of divisions used will give the quantity of titanac acid; the operation may then be continued in the usual manner for estimating the iron.

Another method consists in reducing the iron by sulphuretted hydrogen or sodium sulphide, which does not act on the titanac acid, and then estimating the iron after having freed the liquid from the excess of sulphuretted hydrogen or sulphurous acid in the usual way. The difference gives the amount of titanium. The former method is the more accurate of the two, as the latter frequently gives too much iron.

Separation of Iron from Cerium.

The metals must be in solution in the form of sulphates. Reduce the iron completely to the form of protosulphate by means of a current of sulphuretted hydrogen passed into the hot solution. To the solution, which should be concentrated, add a saturated solution of sodium sulphate, together with a sufficient quantity of the dry sulphate in powder to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sodium sulphates and the cerium metals separate immediately, as a white, highly crystalline powder, which is to be thrown upon a filter and thoroughly washed with a saturated solution of sodium sulphate. After washing, the double sulphates upon the filter are to be dissolved in hot dilute hydro-

chloric acid, the solution largely diluted with water, and the cerium metals precipitated by ammonium oxalate in the manner already pointed out (page 55). From the filtrate the iron may be precipitated at once as sesquioxide by ammonia, after peroxidising it by means of chlorine water, and rendering the solution slightly acid with hydrochloric or sulphuric acid.

Separation of Iron from Magnesium.

When iron sesquioxide is precipitated by means of ammonia from a solution containing magnesium, some magnesium is always carried down with it in spite of the presence of an excess of ammoniacal salts. They may, however, be perfectly separated in this manner:—Dilute the solution considerably, neutralise with sodium carbonate, then add acetic acid and sodium acetate to the cold solution. Boil for a short time, when the whole of the iron will be precipitated as basic acetate. Filter hot and wash quickly with hot water. All the magnesium will be in the solution.

Dr. Calvert dissolves the oxides in hydrochloric and a little nitric acid, nearly neutralises with ammonia, and precipitates the iron with ammonium succinate. The succinate of iron sesquioxide is rapidly filtered off and washed with cold water. The filtrate will contain the whole of the magnesium.

Separation of Iron from Calcium.

When iron sesquioxide is precipitated in the ordinary manner with ammonia in the presence of excess of ammoniacal salts, it always carries down a considerable quantity of lime, if this earth is present, and the larger the proportion of iron as compared with that of calcium, the greater is the proportion of calcium carried down by the iron. This error can be avoided by precipitating the iron as succinate, or by throwing the iron down as basic acetate as just described (Separation of Iron from Magnesium). In either case the whole of the calcium will remain in the solution.

Iron sesquioxide may be safely precipitated by ammonia if the precaution is taken to boil until all smell of ammonia has gone off, before filtering; the iron does not now retain any calcium. If much calcium be present a little ammonium chloride may be added to make sure of getting all into solution. As the solution no longer contains free ammonia, it can be filtered without there being danger of the calcium coming down as carbonate by absorption of carbonic acid from the atmosphere. The filtrate may be concentrated by evaporation, and the calcium precipitated as oxalate.

CHAPTER VI.

MANGANESE, NICKEL, COBALT.

MANGANESE.

CHROMIUM and manganese may be distinguished before the blowpipe as follows, according to Professor E. J. Chapman:—When a mineral is expected to contain manganese it is commonly tested by fusion with sodium carbonate. But chromium compounds form with that reagent a green enamel, much resembling that formed by manganese compounds. The sodium chromate enamel is yellowish-green after exposure to the oxidising flame, and never exhibits any tinge of blue. The sodium manganate enamel is greenish-blue when quite cold. To prevent mistakes the bead may be saturated with vitrified boracic acid until all the carbonic acid is expelled and a clear glass is obtained. The chrome glass will retain its green colour, whilst the manganese glass will become amethystine or violet. In place of boracic acid, silica may be used if more convenient. In this case the reaction is assisted by the addition of a very small amount of borax.

Estimation of Manganese.

Under many circumstances manganese can be estimated with great accuracy by precipitation as ammonio-phosphate, and weighing as pyrophosphate, like magnesium. This salt, from its highly crystalline structure, the facility with which it is formed, and its insolubility, appears well adapted to the quantitative estimation of manganese. Dr. Wolcott Gibbs, who has worked out this method, recommends that to the solution of manganese, which may contain ammonium salts or of the alkaline metals, di-sodic ortho-phosphate is added in large excess above the quantity required to precipitate the manganese as ortho-phosphate. The white precipitate is then to be redissolved in excess of sulphuric or hydrochloric acid, heated to the boiling-point, and ammonia added in excess. A white or semi-gelatinous precipitate is produced, which, on boiling or standing for some time, even in the cold, gradually becomes crystalline, and finally is completely converted into beautiful talcose scales which have a pearly lustre and a pale rose colour. It is best to precipitate each time in a platinum vessel, in which the ammonio-phosphate may be boiled for 10 or 15 minutes, and to allow the salt to remain at a temperature near the boiling-

point of the liquid for an hour after it has become crystalline. The ammonio-phosphate may then be filtered off and washed with hot water. The washing takes place with extraordinary facility on account of the crystalline character of the salt. The ortho-phosphate, after drying and ignition, yields manganese pyrophosphate as a nearly white powder.

The advantage of this method over that commonly employed for the estimation of manganese, is that the process admits of the metal being weighed in the form of a perfectly definite compound, and not as an oxide which cannot be safely assumed to be manganoso-manganic oxide. When manganese is associated with the alkaline earths, it is, of course, first to be separated as sulphide, or as a hydrate of the sesquioxide. The ammonio-phosphate is almost absolutely insoluble in boiling water, in ammonia, and in solutions of ammonium salts. The salt is nearly white, but sometimes becomes a little more red upon the filter. If it assumes a rather deep dull red colour, the whole of the manganese phosphate has not been converted into ammonio-phosphate. The precipitate is then to be redissolved in dilute hydrochloric acid, more sodium phosphate added, and then ammonia in excess, after which the boiling is to be repeated. This repetition is very rarely necessary, a little practice enabling the analyst to judge when the conversion from the flocky-gelatinous to the crystalline condition is complete. The filtrate from the crystalline salt is perfectly free from manganese. This process will not give accurate results in the presence of copper, or of metals which form precipitates with phosphates (see page 182). Phosphoric acid cannot be estimated in this way by precipitation as manganese ammonio-phosphate, because the crystalline character of the salt upon which the success of the process depends is only produced by digestion with an excess of phosphate.

Manganese may be estimated by precipitation as oxalate, and subsequent titration with potassium permanganate (see page 119, Leison's process for the estimation of zinc). To a soluble manganese salt add oxalic acid, and then a large excess of strong alcohol; manganese oxalate is completely precipitated. The subsequent filtration and titration with potassium permanganate is conducted as described at page 119. From the amount of oxalic acid thus found the quantity of manganese may be calculated.

A. Guyard estimates manganese by precipitation with potassium permanganate, which forms, with salts of manganese protoxide, a precipitate of permanganate of manganese protoxide, insoluble in water and dilute inorganic acids. All the other metals whose protoxides react on potassium permanganate are found in the state of peroxide in the same liquor in which the manganese exists as protoxide; consequently, these foreign metals, whatever they may be, do not interfere with the results. As long as there is manganese in the liquor it is precipitated, and the potassium permanganate is decolourised; but as

soon as the reaction is ended a drop of the permanganate communicates a persistent rose tint to the solution.

The operation is best performed in the following manner:—1 or 2 grammes of the salt of manganese to be assayed are dissolved in aqua regia. The solution is boiled for some time to transform all the manganese into a salt of protoxide; the solution is then very nearly neutralised by an alkali; that done, it is diluted with a large quantity of boiling water, and the whole is kept at a temperature of about 80° C. The standard solution of potassium permanganate is now gradually added from a burette. The manganese is immediately precipitated in the form of violet-brown flocculi of manganese permanganate. The operation is arrested occasionally to allow the precipitate to collect, which it does very quickly; and is entirely stopped when a persistent rose colour is obtained.

To estimate the strength of the solution of potassium permanganate use pure sulphate of the manganese protoxide dried at rather a high temperature. This salt has then a fixed composition, and keeps well in a tightly-stoppered bottle. A normal solution may also be prepared for each operation.

For every equivalent of potassium permanganate added, three equivalents of manganese protoxide will be precipitated. In any case the solution must be so prepared that 80 c.c. correspond to about 1 gramme of manganese.

The permanganates of the manganese protoxide are three in number:—

- | | | |
|----|--|-------------------|
| 1. | The oxide Mn_2O_3 , the formula of which should be written | $5MnO, Mn_2O_3$. |
| 2. | " Mn_2O_4 " " " " | $4MnO, Mn_2O_4$. |
| 3. | " Mn_2O_5 " " " " | $3MnO, Mn_2O_5$. |

Each of these bodies is formed, according as we mix 1 equivalent of potassium permanganate with 5, 4, or 3 equivalents of a salt of the manganese protoxide. The first is formed in the cold when there is more manganese salt than potassium permanganate; the second is also formed in the cold when more permanganate than manganese salt is present in the solution. The binoxide is only formed in a hot solution.

Munroe estimates manganese as pyrophosphate. The solution of a manganic salt is boiled for 5 minutes in the water-bath with an excess of sodium pyrophosphate; the precipitate is dissolved in a minimum of hydrochloric acid, and then boiled for 15 minutes with ammonia, avoiding excess. The precipitate is redissolved in hydrochloric acid, reprecipitated with ammonia, and the white crystalline precipitate, which turns partially brown on exposure to the air, is boiled for more than an hour. Mere traces of manganese remain in the filtrate. An excess of ammonia makes the result inaccurate. The precipitate is treated exactly like the corresponding magnesian precipitate.

Mr. John Pattinson finds that the whole of the manganese in a solution of manganous chloride can invariably be precipitated in the condition of dioxide, if a certain amount of *ferric chloride* be present, by a sufficient excess of a solution of calcium hypochlorite or bromine-water, adding, after heating the solution to from 140° to 160° F., an excess of calcium carbonate, and then well stirring the mixture. Without the ferric salt the precipitation as dioxide is imperfect. Zinc chloride may be substituted for ferric chloride, but neither aluminium nor barium chlorides have the same desirable effect. The author recommends the following solutions, &c.:—The clear liquid obtained by decantation from a 1·5 per cent. solution of bleaching-powder; light granular calcium carbonate obtained by precipitating an excess of calcium chloride by sodium carbonate at 180° F.; a 1 per cent. solution of ferrous sulphate in dilute (1 in 4) sulphuric acid; standard solution of potassium dichromate equivalent to 1 part of iron in 100 of solution. The application of the process to manganiferous iron ores is as follows:—10 grains of the ore, dried at 212°, are dissolved, in a 20-ounce breaker, in about 100 fluid grains of hydrochloric acid (sp. gr. 1·18). Calcium carbonate is then added until free acid is neutralised and the liquid turns slightly reddish. 6 or 7 drops of hydrochloric acid are now added, and 1000 grains of the bleaching-powder solution, or 500 grains of saturated bromine-water, and boiling water run in until the temperature is raised to 140° to 160° F.; 25 grains of calcium carbonate are added, and the whole well stirred. If the supernatant solution has a pink colour, the permanganate is reduced by a few drops of alcohol. The precipitated iron and manganese oxides are filtered off and washed. 1000 grains of the acidified ferrous sulphate solutions are carefully measured into the 20-ounce beaker already used; the filter with its washed contents added. A certain quantity of the ferrous sulphate is oxidised by the manganese dioxide; this quantity is estimated with the standard dichromate solution, when the quantity of manganese dioxide can easily be calculated. The iron present must be at least equal in weight to the manganese during the precipitation, in order to ensure the absence of lower oxides.

Professor J. Volhard, for the separation and estimation of manganese, makes use of a standard solution of potassium permanganate, which he prepares by dissolving 88·5 grammes crystals of permanganate in about 2 litres water in a boiling-flask. The solution is poured into a well-stoppered bottle which holds 10 litres, filled up to the mark with water and well mixed by shaking. This store is kept in a dark place. To fill the burettes, the author uses a 1-litre washing-bottle with a wide mouth covered with black paper. Before filling this vessel out of the stock-bottle, it is several times washed out with a little of the solution. The value of the permanganate solution is then estimated, which is best effected by iodine. For this purpose there are required a solution

of sodium thiosulphate and a starch solution, both of known strength, besides a solution of potassium iodide and one of starch.

The reducing liquid is obtained by dissolving 30.061 grammes pure crystalline sodium thiosulphate along with about 8 grammes ammonium carbonate and making up to 1000 c.c.; 1 c.c. of this solution = 2 milligrammes manganese. To prepare the iodine solution, 1.5894 gramme dry iodine in crystals is dissolved in a little water by the aid of 8.5 potassium iodide, and made up to 1000 c.c.; 10 c.c. of this solution are reduced by 1 c.c. of the thiosulphate solution. The potassium iodide solution should contain per litre 55 grammes potassium iodide free from iodate. The solution of starch is prepared fresh daily.

About 10 c.c. of potassium solution are placed in a beaker, 4 to 5 c.c. pure hydrochloric acid with 150 to 200 c.c. water are added, and constantly stirring, about 20 c.c. of the permanganate solution are added from a Gay-Lussac burette. The beaker is then placed under a Mohr's burette containing the thiosulphate solution, and some of this is added till the brown colour of the iodide solution is changed to a faint yellow. Starch solution is now added, and thiosulphate again till the blue colour is completely destroyed. In order to estimate the small excess of thiosulphate which has been added, solution of iodine is added with a small graduated pipette till the blue colour just reappears. The volume of thiosulphate consumed, less one-tenth of the iodine solution used, and divided by the volume of the permanganate solution, gives the factor of the permanganate: 1 c.c. permanganate indicates 2 milligrammes \times factor for manganese.

The standard of the thiosulphate solution should be checked from time to time. For this purpose the author uses a liquid prepared by dissolving 5.963 grammes potassium dichromate, and making up to 1000 c.c. Of this solution 1 c.c. gives up to hydriodic acid exactly as much oxygen as the quantity of permanganate, which indicates 2 milligrammes manganese; 20 c.c. of the chromate solution are measured off with a pipette, and let flow into the acidified solution of potassium iodide, proceeding exactly as directed above for standardising the permanganate. If more than 20 c.c. of the thiosulphate are used for reducing the iodine set free the thiosulphate was impure.

Any other permanganate solution of known strength will serve as well for the titration of manganese, and if a solution is kept in stock for the titration of iron, it would be superfluous to prepare another. It must be remembered, however, that only three-fifths of the oxygen in the permanganate, indicated by ferrous oxide, oxalic acid, or hydriodic acid, come into play in the oxidation of manganous oxide. The manganese standard may be found by multiplying the iron standard by 0.2946.

For the titration of manganese, if iron is absent, or present only in a small quantity, the solution of the manganese salt is rinsed into a long-necked boiling-flask, with the addition of 1 gramme zinc sulphate,

and diluted so that 100 c.c. may contain not more than about $\frac{1}{2}$ gramme manganese. If the solution is neutral, 2 or 3 drops of pure nitric acid are added (1·2 sp. gr.); if acid, it is first neutralised with pure sodium carbonate till a permanent precipitate begins to appear, then acidified with 3 or 4 drops of nitric acid and heated to a boil. The flask is taken from the flame and the permanganate run in with the burette, promoting the collection of the precipitate by vigorous shaking. The redness which appears towards the end repeatedly disappears again on further agitation. If fine reddish-brown flocks remain suspended in the liquid, so that it does not become thoroughly clear and transparent, the flask is set for a few minutes on a very gentle flame, but not allowed to boil.

The flocks become more compact and subside on shaking. The liquid at the end of the operation must have a distinct rose colour, which must remain after repeated shaking. The zinc sulphate must be carefully tested; its dilute solution should not, on boiling, destroy the colour of a drop of permanganate.

Metallic alloys, such as cast iron and steel, are dissolved for the determination of the manganese in dilute sulphuric acid with the addition of nitric acid. The solution is effected in a litre flask, heated on the water-bath. In a mixture of 8 volumes dilute sulphuric acid (1·18 sp. gr.) and 1 volume nitric acid (1·4 sp. gr.) common bottle-wire, on heating in the water-bath, dissolves in 5 or 6 minutes without violent evolution of gas. The digestion must be prolonged in order to convert the iron completely into oxide. Many ores and slags can only be dissolved by the aid of hydrochloric acid, in which case, after the oxidation of the iron, the hydrochloric solution is mixed with concentrated sulphuric acid and evaporated in a porcelain capsule, first in the water-bath and then in the gas-stove, till the sulphuric acid begins to escape. The mass is then rinsed with water into the litre-flask. The more highly carburetted cast iron, spiegeleisen, and ferro-manganese are dissolved in nitric acid in a small flask; the solution, without filtration, is rinsed into a porcelain capsule, evaporated to dryness in the water-bath, and heated in the gas-stove to the complete decomposition of the nitrates, whereby the carbonaceous matters are burnt. The residual oxides are digested with hydrochloric acid in a covered capsule on the water-bath, when the oxides dissolve. The hydrochloric acid is then again expelled by heating with sulphuric acid.

The bulk of the acid is next neutralised with pure sodium carbonate or hydroxide. Zinc oxide suspended in water is then added till all the iron is thrown down, which is ascertained by the circumstance that the solution suddenly coagulates and the supernatant fluid becomes milky. The flask is then filled up to the mark with water, allowed to settle for some minutes, and filtered through a dry folded filter into a dry vessel. A part of the filtrate (200 c.c.) is placed in a boiling-flask, acidified with 2 to 4 drops nitric acid and heated to a boil. The flask is then

taken from the fire, and the permanganate run in with the burette. The titration can be repeated with a second and a third portion of the liquid.

For the estimation of small quantities of manganese M. T. M. Chatard makes use of Crum's test:—A standard solution of ammoniac oxalate is prepared of which 1 c.c. = 0.0005467 gramme manganese. A sample of dolomite is taken, dissolved in nitric acid, and a small quantity of plumbic peroxide added. On boiling, the bright colour of permanganic acid appears. The solution is passed through small filters of asbestos with the aid of a Bunsen's pump, and the permanganic acid is estimated by means of a standard solution of ammoniac oxalate. This method, though giving good results where the percentage of manganese is small, fails when any large amount of that metal is present.

M. A. Leclerc proposes the following process for the estimation of manganese in soils and in the ash of plants. It consists in the conversion of manganese nitrate into a permanganate, and the titration of the latter by means of a suitable solution. The conversion just mentioned is readily effected by the aid of red-lead, because the iron and aluminium, the only substances which could react upon the permanganate, are at the time of the conversion already peroxidised. The reaction alluded to will always succeed, provided there be no chlorine present in the substances employed.

Before detailing the quantitative operation, it is necessary to describe the practical details of the experiments. When a soil (arable or other) is to be operated upon by nitric acid, it is first necessary to destroy the organic matter it contains by igniting the soil to red heat. It is next boiled with nitric acid, care being taken not to evaporate the solution to dryness, since owing to the fact that the manganese nitrate is decomposed, at 142° , into manganese dioxide, which is insoluble in nitric acid, manganese might be lost. When the nitric acid appears to have taken up all the manganese the liquid is filtered, and then diluted with water up to a given and determined bulk. A fraction of this fluid, viz. that in which the chlorine has been estimated by means of silver nitrate, is next boiled in a porcelain capsule, and after boiling some red-lead is added, care being taken to stir the fluid. The result is that the fluid assumes a beautiful violet colour, due to potassium permanganate, the colour being somewhat masked by that of the lead peroxide, which is simultaneously formed and deposited in an insoluble condition. The depth of the violet colouration depends upon the greater or less amount of manganese present. If it should happen that the red-lead be not acted upon, it is due to the liquor not being sufficiently acid, and consequently some more nitric acid will have to be added. The lead peroxide having been precipitated, the liquor is filtered through asbestos free from chlorine. The filtrate is then ready for titration, the liquid containing a slight excess of nitric acid, potassium

permanganate, lead nitrate, iron, alumina, magnesia, lime, sodium, and potassium salts. Titration by means of the double iron and ammonium sulphate is out of the question, because the formation of lead sulphate would prevent the end of the reaction from being seen, and oxalic acid cannot be used, both on account of its giving rise to the formation of lead carbonate, and because it requires a higher temperature. The author, therefore, looked for another reducing agent which would allow him to observe correctly the change of the violet to another colour: mercury subnitrate was found to answer the purpose in this respect. This salt is rapidly converted into mercury pernitrate by the permanganate, and the end of the reaction is marked either by a yellowish-green colouration, when much manganese is present, or by complete decolouration of the fluid if only a little of the metal is present. The solution of mercury subnitrate does not form any precipitate, unless, indeed, too much manganese were present, but care should be taken that the liquid to be titrated is rather freely acid, because otherwise manganese sesquioxide is thrown down. The solution of mercury subnitrate is first titrated by means of permanganate.

M. A. Guyard (Hugo Tamm) finds that from the neutral or slightly acidulated mixture of manganese and ammonium chlorides, manganese can be thoroughly precipitated in the state of manganese carbonate, by means of a slight excess of ammonium carbonate.

In these conditions manganese is precipitated as the ordinary manganoous carbonate, and the precipitation thus effected is so perfect that in the filtrate it is quite impossible to discover a trace of manganese by means of ammonium sulphide. Indeed the precipitation of manganese by ammonium carbonate, effected under the conditions prescribed, is safer than by means of ammonium sulphide.

The precipitated manganese carbonate is allowed to settle in a warm place (boiling not being required), and the whole is filtered. The manganese carbonate thus obtained is a little denser than the one precipitated by sodium carbonate, and it can be washed with facility with hot water, and if a double filter is used no trace of the precipitate passes through the filters. After drying, the precipitate is calcined, and manganese is estimated as usual in the state of the oxide Mn_2O_4 .

Detection of Manganese in Ashes.

Professor E. Campani proceeds thus:—When there are sufficient phosphates in the ash it is treated with an excess of hot aqua regia, the liquid filtered, and evaporated to dryness in a porcelain capsule on the water-bath. If the ash contains manganese the residue presents an amethyst or violet colour, more or less intense, according to the quantity of the manganese phosphate produced. As all ashes do not contain phosphates, the author finds it useful to treat with a mixture of 15 c.c. of syrupy phosphoric acid and 85 c.c. of nitric acid.

Separation of Manganese from Zinc, Nickel, and Cobalt.

After separating manganese from certain groups of substances easy of separation, manganese may still be mixed with zinc, nickel, and cobalt, and the separation of these substances is rather troublesome, but some of them are simplified by the use of the ammonium carbonate process.

When manganese is precipitated by ammonium carbonate from the slightly acidulated mixture of manganese and ammonium chlorides, if cobalt is present, part of this metal is precipitated in the state of carbonate along with the manganese carbonate, to which it imparts a pink colour, and part of it remains in solution. Consequently the separation of manganese from cobalt cannot be effected by means of the ammonium carbonate process. But when zinc or nickel, or both metals, are present, the separation of these two metals is effected with perfection, manganese being precipitated as carbonate, and both zinc and nickel remaining in solution. This reaction is rather important, for it is not unfrequently the case that manganese, nickel, and zinc exist in the same liquor, and their usual modes of separation are rather complicated, and this process simplifies them.

Estimation of Manganese in Manganese Ores.

The chief use of a mode of estimating manganese is for the valuation of manganese ores. If the ore is contaminated with calcium carbonate, it is first treated with very weak cold nitric acid, which dissolves this substance without attacking sensibly the manganese oxide, and after a few washings it is treated as an ore containing no calcium carbonate, as follows:—From 20 to 50 grains of the ore are dissolved in hydrochloric acid, and the mixture is heated until the chlorine evolved is thoroughly disengaged. The solution thus obtained is diluted with water and filtered in order to collect the insoluble residue, and after being carefully neutralised by ammonia, with the usual precautions, it is precipitated by means of ammonium succinate. Both iron and alumina are precipitated. The mixture is filtered, and to the clear liquor a slight excess of ammonium carbonate is added. Manganese is thus precipitated completely in the state of carbonate. This precipitate is allowed to settle in a warm place, it is then collected on a filter, washed, dried, and calcined, and manganese is estimated as the oxide Mn_2O_4 .

Valuation of Manganese Ores.

The best methods used for the valuation of manganese ores are not necessarily those which give in the most rapid and accurate manner the absolute amount of manganese peroxide present in the ore. The analyst must bear in mind that the commercial value of manganese ore depends on its power of liberating chlorine from hydrochloric acid; and it not unfrequently happens that an ore, which on accurate

analysis would be reported to contain a high percentage of manganese peroxide, likewise contains some other mineral (protioxide or magnetic iron oxide), which will materially reduce the value of the manganese as a chlorine-yielding ore. It is on this account that some processes—excellent though they be from a purely analytical point of view—have fallen into discredit amongst manufacturers, whilst other processes which do not profess to give the amount of manganese peroxide *actually* present, but only that *available* for liberating chlorine, are now generally adopted. In the following pages are given the methods of testing manganese ore for the available peroxide which have best stood the test of practical experience.

Messrs. Scherer and Rumpf, after examining all the most approved methods in Dr. Fresenius's laboratory at Wiesbaden, have come to the conclusion that Bunsen's method is the best for rapidly giving the amount of available manganese in an ore. This process is carried out by dissolving a weighed quantity of the sample in strong hydrochloric acid in a small flask, until complete decomposition has taken place. The escaping chlorine is received in a strong solution of potassium iodide, and the liberated iodine subsequently estimated by means of a standard solution of sodium thiosulphate and a solution of starch. To prevent the solution of potassium iodide from being sucked back into the generating-flask, a few small pieces of magnesite are introduced with the manganese, so that a continual slight escape of carbonic acid takes place through the solution. The solution of sodium thiosulphate is tested by means of carefully prepared pure iodine, dissolved in potassium iodide. The solution should be of such a strength that 1000 c.c. of sodium thiosulphate solution corresponds to from 2 to 8 grammes of manganese peroxide. In this estimation the iodine liberated by the chlorine should be tested as soon as possible after the decomposition; it gives higher results after standing 24 hours than before. These higher results are caused by the liberation of iodine by spontaneous decomposition of hydriodic acid, set free by hydrochloric acid, distilled over during the process. The following experiment proves this:—A few drops of hydrochloric acid were added to a solution of potassium iodide. The solution remained for some hours colourless, but, after standing 24 hours, had become quite yellow, and was found to contain free iodine sufficient to indicate 8 per cent. of manganese peroxide when titrated with thiosulphate.

Messrs. Scherer and Rumpf have made the suggestion that the value of manganese ores should be measured by chlorometrical degrees rather than by the actual percentage of binocide; thus tending in the same direction as the resolution¹ passed by the Association of Alkali Manu-

¹ 'That, as the testing of manganese, according to the method of Will and Fresenius, is, in the opinion of the meeting, incorrect, and yields uncertain results, it is recommended to members of this Association not to buy by that test.'

facturers in 1869, in reference to this subject—a decision which would seem also to indicate a desire on the part of manufacturers that tests of manganese ore should express the amount of peroxide *available* for liberating chlorine, and not the amount *actually* present in the ores.

For the above reasons, Dr. Paul adopts Mohr's method of using a known quantity of a standard solution of oxalic acid, together with excess of sulphuric acid, for dissolving the ore; if necessary, boiling until the ore is completely dissolved, and then, by means of a standard solution of permanganate, determining the quantity of oxalic acid remaining undecomposed. This method is very convenient for testing manganese ores, and involves only one weighing for each test. The results obtained are also very uniform.

This method has also the advantage of giving results which fairly represent the amount of available peroxide in manganese ores; for any iron that may be present as metal or protoxide would consume an equivalent quantity of permanganate solution, and thus apparently reduce the quantity of oxalic acid decomposed by the peroxide to an extent proportionate to the amount of iron existing in the ore. Thus, for instance, if the quantity of oxalic acid decomposed by 100 grains of manganese ore free from iron or iron protoxide were 109.58 grains, the ore would contain 76.5 per cent. of peroxide, and the whole of that would be available. But, if the 100 grains of ore also contained 5.6 grains of metallic iron, or an equivalent of protoxide, the permanganate solution required for peroxidising that iron would represent 6.8 grains of oxalic acid, and the quantity of oxalic acid decomposed by the peroxide would appear so much less than it really was, or 108.28 grains instead of 109.58 grains. Accordingly, the amount of peroxide would be represented as 72.1 per cent., instead of 76.5 per cent.; and that would, in fact, be the amount of peroxide available for generating chlorine.

This method of testing recommends itself by its simplicity, and by the fact that the standard solutions of oxalic acid and permanganate will keep for a long time without alteration of value. The oxalic acid solution contains 68 grammes in the litre, and 1 c.c. is equivalent to 5 c.c. of the permanganate solution.

Mr. John Pattinson prefers a modification of Otto's process for the valuation of manganese, which consists in boiling the ore with a known weight of a proto-salt of iron, and then estimating the excess of iron by a standard solution of potassium bichromate. This modified process, in his opinion, requires less skill and care at the hands of the operator than Bunsen's method, as described by Messrs. Scherer and Rumpf. 80 grains of clean iron wire are placed in a 20-ounce flask, along with 8 ounces of dilute sulphuric acid, made by adding 8 parts of water to 1 of oil of vitriol. A cork, through which passes a tube bent twice at right angles, is inserted in the neck of the flask, and the flask is heated over a gas flame until the iron is dissolved. The bent tube is

placed so as to dip into a small flask or beaker containing a little water. When the iron is quite dissolved, 80 grains of the finely-powdered and dried sample of manganese ore to be tested are put into the flask, the cork replaced, and the contents again made to boil gently over a gas flame until it is seen that the whole of the black part of the manganese is dissolved. The water in the small flask or beaker is then allowed to recede through the bent tube into the larger flask, more distilled water is added to rinse out the small flask or beaker and bent tube, the cork well rinsed, and the contents of the flask made up to about 8 or 10 ounces with distilled water. The amount of iron remaining unoxidised in the solution is then ascertained by means of a standard solution of potassium bichromate. The amount the bichromate indicates, deducted from the total amount of iron used, gives the amount of iron which has been peroxidised by the manganese ore, and from this can be calculated the percentage of manganese peroxide contained in the ore. Thus, supposing it were found that 4 grains of iron remained unoxidised, then $80 - 4 = 26$ grains of iron, which have been oxidised by the 80 grains of ore. By a simple calculation it is found that these 26 grains of iron are equivalent to 20·48 grains of manganese peroxide, the amount of peroxide in the 80 grains of ore. The percentage is, therefore, 68·10.

It will be seen, from the above description, that the only differences between this method and that usually described in handbooks are the use of sulphuric acid instead of hydrochloric acid, and the dispensing with the use of a stream of carbonic acid. These alterations, however, enable us to get rid of the source of error caused by the evolution and escape of a little chlorine, and also of the somewhat complicated and troublesome apparatus required to supply a stream of carbonic acid.

The use of sulphuric acid instead of hydrochloric acid not only gets rid of the before-mentioned source of error, but it is also the reason why the carbonic acid atmosphere can be dispensed with. It has been ascertained that the solution of iron in sulphuric acid does not oxidise appreciably by exposure to air within any reasonable time; certainly not within the time required to make the test. The solution of iron in hydrochloric acid oxidises much more rapidly.

The kind of iron wire which answers best for these analyses is that used by wire-workers, and known as 'annealed iron wire.' Only the purest qualities of iron are used for wire of this description. Carefully examined by comparing it with pure oxalic acid and pure potash bichromate, as well as by heating it in an atmosphere of chlorine, it is found to be within about 0·1 of a per cent. of being absolutely pure, so that for all practical purposes of testing it may be considered pure. There is no difficulty in obtaining it in large quantity and of uniform quality. Wire of this kind, of such thickness that 22 wires laid close together cover an inch, is of equally pure quality with that which requires about 85 wires to the inch. The latter is, however, to be preferred, because it

is more easily cut and dissolved. Pianoforte wire, which is made of steel, will not do, excepting a correction is made for the amount of carbon it contains. Mr. Pattinson says that he has found wire of this kind which contains not more than 98.5 per cent. of pure iron. The odour of the hydrogen evolved during solution is a good indication of the purity of the iron. With steel wires the odour of carburetted hydrogen is very strong, but with the annealed iron wire it is very slight. In all cases it will be desirable to ascertain the purity of every new batch of iron wire obtained previous to its being used for testing manganese ores. Having once obtained wire of known purity, all future batches may be most easily and correctly tested by comparing the amount of manganese peroxide, and consequently of iron, indicated by a certain ore when tested by the new wire with the amount indicated when tested by the wire of known purity. The wire is easily cleaned from all adhering oxide and dirt by passing it a few times through fine emery paper and afterwards through a cloth. It is dissolved by the sulphuric acid in about 15 minutes. Crystals of iron protosulphate, or of the double iron and ammonium sulphate, are not recommended, on account of the uncertainty of their composition, as they are never met with in so pure a condition as the iron wire. Besides, there is no advantage in their use; it is quite as easy to weigh the iron wire as to weigh crystals of iron protosulphate. A standard solution of iron protosulphate does not keep sufficiently well to make it worth while to use this.

The use of the small flask or beaker in connection with the bent tube is to prevent all loss of iron by its being carried over with the hydrogen and steam. Occasionally a slight trace of the iron has been thus carried over through the tube, but this is, of course, all arrested by the water in the small beaker or flask, and is again returned into the larger flask when the tube is rinsed out.

The length of time required to decompose the manganese ore depends upon the hardness of the sample under examination, and this mode of testing thus affords a good indication of the nature of the ore in this respect. Soft ores will be decomposed in a minute or two, whilst very hard ores require 15 minutes or more. The decomposition can be hastened by adding more oil of vitriol, but this must be done after the iron is dissolved, as the latter does not readily dissolve in stronger acid than that above mentioned.

The standard potassium bichromate solution is made so that 1000 fluid grains will peroxidise 10 grains of iron. It is applied to the diluted solution in the usual way. If there is reason to suppose that the ore to be tested contains more than about 78 per cent. of peroxide, it will then, of course, be necessary to use less than 80 grains of ore or more than 80 grains of iron; as these quantities are only intended for ores of a lower percentage than about 78.

Referring to the discrepancies in the results of analysis of manga-

nese ore, especially that imported from Spain, which have been noticed, according as the method of quantitative estimation of manganese peroxide employed was that of Fresenius and Will, or that known as the iron test, Dr. Mohr says that the cause of this discrepancy is due to a certain amount of magnetic iron oxide present along with the manganese ore. Since the magnetic iron oxide interferes in the same manner when such a manganese is employed for the manufacture of chlorine, and since the quantity of the gas set free is only that which remains after the oxidation of the magnetic iron ore, the manufacturer who purchases such manganese should be asked to pay for that article only its value as manganese peroxide. It, however, frequently occurs that the mining and manufacturing interests here clash, and that, as a consequence, the ore proprietor will desire the value of his material to be estimated by the method of Fresenius and Will, while the manufacturer prefers that of the iron test. That right as well as equity are on the manufacturer's side is clear from the following instance:—Suppose the ore contains a mixture of 1 atom manganese peroxide and 2 atoms magnetic iron ore, or 27·8 per cent. of the former with 72·7 per cent. of the latter; in such a mixture the method of Fresenius and Will will indicate with precision the amount of manganese peroxide, but on adding hydrochloric acid to this mixture not a trace of chlorine will be given off, since the free atom of oxygen of the manganese peroxide is just sufficient for the oxidation of the 2 atoms of iron protoxide of the magnetic iron ore; in the same way a mixture of manganese binoxide with iron protosulphate or protocarbonate of that metal will be perfectly worthless as an article for chlorine-making.

Dr. Mohr accordingly recommends that manganese ores and samples of manganese peroxide should be always tested, previous to analysis, with an astatic magnetic-needle, and he further recommends Dr. Bunsen's process (given on page 239) as the best and surest method of analysis. This process is really the same as that which the manufacturer employs for making chlorine; any magnetic iron ore present will become oxidised in both processes, and a special examination for magnetic iron oxide is rendered unnecessary, while the available manganese for the production of chlorine only is estimated.

Separation of Manganese from Iron.

Obtain the two metals in the form of chlorides (iron sesquichloride and manganese protochloride), dilute the solution considerably, and neutralise as nearly as possible with sodium carbonate. To the cold solution add sodium acetate in more than sufficient excess to change all the iron and manganese by double decomposition to neutral acetates. Add a few drops of acetic acid. Raise to the boiling-point and keep in brisk ebullition for a short time, and then filter rapidly through a ribbed filter, keeping the liquid as hot as possible during filtration. The whole of the iron will be in the precipitate as basic acetate, whilst

the manganese will be in solution. If an absolutely complete separation is needed, redissolve the precipitate in hydrochloric acid, and repeat the operation. Traces of manganese, which the first precipitate of basic iron acetate may have carried down, are in this manner removed. The two filtrates containing manganese may be added together.

Ammonium succinate added to a neutral solution of iron sesquichloride and manganese protochloride entirely precipitates the iron. Filter off and wash with cold water; all the manganese will be in the filtrate.

Barium carbonate added gradually, with constant stirring, to a similar solution, precipitates all the iron as sesquioxide.

To a similar solution, which must be acid and cold, add solution of sodium carbonate, drop by drop, with constant stirring, till the iron sesquioxide is entirely precipitated, then filter; the manganese will be held in solution by the excess of carbonic acid in the liquid. Of these methods we have found the one first described the most accurate.

For other methods, see page 180 (Estimation of Manganese in Iron), page 195 (Analysis of Blister Steel), page 197 (Analysis of Spathic Iron Ore), and page 206 (Special Methods for Analysis of Iron Ores).

Direct Separation of Manganese and Iron.

Pour the solution of the two metals into an excess of a concentrated aqueous solution of potassium cyanide. After standing from half an hour to an hour the precipitate redissolves, and only a slight turbidity remains. The whole is filtered, the residue is dissolved in a few drops of dilute hydrochloric acid, the solution is mixed with excess of potassium cyanide, and the clear solution is added to the filtrate. All these operations are performed in the cold. Solid iodine is then added till the liquid appears brown, when any traces of free iodine are removed by the addition of a few drops of free alkali. The complete separation of the manganese is ascertained by adding iodine to a small portion of the liquid, decanted or filtered; heating very gently and adding sodalyle. The liquid should remain clear. The precipitated manganic oxide is filtered off, washed, dissolved in hydrochloric acid, precipitated with ammonium sulphide at a boil, and weighed as manganese sulphide.

The salts of the two metals are dissolved in concentrated nitric acid (1.35), heated to a boil and kept at this temperature, whilst potassium chlorate is gradually added in small portions. The liquid is diluted with water and filtered. The precipitate, when washed, is always found to contain iron. It is therefore redissolved in hydrochloric acid, evaporated to dryness, and the residue taken up in concentrated nitric acid, and treated again with potassium chlorate at a boil. A peroxide is now precipitated containing very small traces of iron.

Separation of Manganese from Aluminium.

Manganese and aluminium may be separated by employing a similar process to the one first described for the separation of manganese from iron (page 249, with sodium acetate), bearing in mind that the precaution of dissolving the precipitated basic aluminium acetate, and re-precipitating it by treatment with sodium acetate as there advised, should always be adopted, since aluminium has more tendency than iron to carry down manganese.

Another process consists in adding ammonium chloride, heating to ebullition, pouring in caustic ammonia, and boiling till the excess of the latter is disengaged. The small quantity of manganese protoxide at first carried down decomposes the ammonium chloride upon ebullition and dissolves as chloride, the ammonia going off. When no more smell of ammonia is perceived, the solution may be filtered without taking special precautions against free access of air.

Separation of Manganese from Zinc.

Obtain the solutions in the form of protochlorides, nearly neutralise with sodium carbonate, dilute with a large quantity of hot water, and keep the solution at about 80°C . Add solution of potassium permanganate until the supernatant liquid is of a persistent rose-colour. All the manganese will be in the precipitate in the form of manganese permanganate or manganese binoxide, whilst the zinc will be in solution. If the strength of the solution of potassium permanganate has been previously ascertained, the manganese may be determined in this way quantitatively (see page 281); if not, the precipitate may be filtered off, calcined, and weighed as Mn_2O_4 . Three-fifths of the total quantity of manganese found will represent the amount originally in solution.

Separation of Manganese from Uranium.

This separation may be effected by means of potassium permanganate in the same way as that of manganese from zinc as above described.

Separation of Manganese from Cerium.

This is best effected in the same way as the separation of iron from cerium (page 228).

Separation of Manganese from Magnesium.

To separate manganese from magnesium, the best plan consists in adding a solution of sodium acetate, heating, and passing a current of chlorine through the liquid, when permanganate is formed. Saturate with ammonia, and boil, when all the manganese is reduced to sesquioxide and precipitated, whilst the magnesium remains in

solution. If there be a large quantity of magnesium present, a certain quantity of sal-ammoniac must be first added.

The same process will serve to separate lime from manganese protoxide.

NICKEL.

Preparation of Metallic Nickel.

Nickel can easily be precipitated as a coherent metallic sponge, by placing a solution of a pure nickel salt in contact with metallic magnesium in the form of ribbon. Hydrogen is given off, and if the materials are pure the nickel will likewise be pure. The sponge is to be well washed with hot water, dried, and then compressed in a steel mortar, when it will assume a metallic brilliancy. Nickel precipitated in this manner can be moulded and condensed by pressure into bars, which will be found to possess magnetic properties like iron. This compressed sponge can be melted in a lime crucible before the oxy-hydrogen blowpipe (see Iron, page 192).

Estimation of Nickel.

In precipitating nickel from its solutions by means of ammonium sulphide, the analyst is frequently troubled by the nickel sulphide dissolving in the excess of precipitant, colouring it brown. This can be completely avoided by employing ammonium sulphide fresh and free from polysulphide. A more satisfactory plan is to saturate the solution of nickel with sulphuretted hydrogen, and then to add ammonia to slight alkaline reaction. The precipitate is then filtered off as rapidly as possible, and washed with dilute sulphuretted hydrogen water. If this precipitation is for quantitative purposes, it must be remembered that when the nickel sulphide is ignited, some of the sulphur goes off, whilst another part oxidises and remains as nickel sulphate, the result being a variable mixture of disulphide, sulphate, and nickel oxide. Forbes has examined this reaction and has based upon it an ingenious plan for estimating nickel. As the equivalent of the sulphur in the nickel sulphide and of the oxygen in the oxide are identical, the sulphide and the oxide will be of the same weight, and this fact enables us at once to calculate the amount of nickel contained in a mixture of the disulphide and oxide, however variable the relative proportions of these compounds may be, and it becomes only necessary to remove the small amounts of sulphuric acid present in the incinerated sulphide in order to determine the amount of nickel present. The addition of a small amount of pulverised ammonium carbonate to the incinerated sulphide as soon as it is cold, and then carefully heating until all ammoniacal salts are expelled, completely effects this object. In estimating the nickel present the calculation may be made as if the calcined mass were either all disulphide or all oxide.

It will be found most convenient to add the ammonium carbonate

to the incinerated sulphide in the same crucible in which it has been ignited, or rather to cover the ignited sulphide with four or five times its volume of this salt, and then, by means of a small agate pestle or glass rod, to break up all grains and mix well together by trituration; this can easily be effected without any loss whatever, as the superstratum of ammonium carbonate effectually prevents any particles flying over the sides of the crucible. This, with its cover loosely placed upon it, is now very gently heated until nearly all ammoniacal salts are expelled: then the heat is increased for an instant, and the whole, after cooling over sulphuric acid, is weighed and estimated as usual.

Nickel may be very accurately determined by Leison's oxalic acid process, for details of which see page 119. In the case of nickel sulphate it is necessary, after adding the oxalic acid, to concentrate the mixture on a water-bath before adding alcohol, and then further to digest for about half an hour, replacing the alcohol as fast as it evaporates. The oxalate is collected on a paper filter, and after washing, dissolved in ammonia on the filter. The filtrate is then acidified with sulphuric acid, when it is ready for titration with potassium permanganate. But the solution containing nickel sulphate has a green colour, which would interfere with the delicacy of the permanganate test, and to overcome this difficulty an ingenious artifice may be adopted, first employed, we believe, by Dr. W. Gibbs, and based on an observation of Maumené. The colours of cobalt and nickel are exactly complementary one to the other, so it is only necessary to add gradually a solution of cobalt sulphate to the green nickel solution, when the colour of the latter is gradually discharged, finally giving place to a neutral tint, which in no way interferes with the delicacy of the permanganate colour test. Although the object is to ascertain the amount of nickel present, this is really effected by estimating the quantity of oxalic acid which was united with it, therefore the addition of cobalt at this stage of the process does not interfere.

For the estimation of nickel in ores, A. A. Julien directs to digest from 8 to 5 grammes of finely powdered ore with 20 c.c. sulphuric acid, 10 c.c. nitric acid, and 5 c.c. hydrochloric acid. Evaporate to dryness, expelling the excess of sulphuric acid, cool, moisten with hydrochloric acid, add hot water, filter, and wash. Saturate the diluted filtrate with sulphuretted hydrogen gas, filter out the copper, lead, &c. sulphides, and wash with sulphuretted hydrogen water. Boil the filtrate with a little nitric acid, add sodium carbonate almost to neutralisation, and precipitate the iron and alumina as basic acetates, as in the analysis of iron ore; filter and wash. Dissolve the basic acetates in hydrochloric acid and repeat the precipitation, filtration, and washing, to separate a little nickel at first carried down. Unite and concentrate all the filtrates and washings, and add ammonia in excess. If a little iron separates, filter, wash twice, dissolve in hydro-

chloric acid, reprecipitate with ammonia, filter, wash, and add the filtrate to the main solution. Boil, add a boiling solution of sodium sulphide in excess, acidulate with acetic acid, allow to settle, filter, wash the nickel sulphide with sulphuretted hydrogen water, remove the moist precipitate as completely as possible to an evaporating-dish; dry, and burn the filter; dry and roast the precipitate in the dish, and add the ashes of the filter. Dissolve the whole in a little aqua regia, evaporate the free acid almost entirely, dissolve in hot water, boil, add pure solution of potash in slight excess, heat for some time nearly to ebullition, decant upon a filter 3 or 4 times, boiling up each time, filter, wash thoroughly with hot water, dry, ignite, and weigh as mixed nickel and cobalt oxides. Carefully examine the residue for potash, silica, iron, alumina, and cobalt.

In American ores, the metal in this residue rarely exceeds 1 per cent. of the original ore, and the cobalt is seldom separated; but, if desired, the following method may be employed:—

Dissolve the residue in a few drops of nitric acid and neutralise the excess of free acid with a few drops of potash. Then add a concentrated solution of potassium nitrite (previously neutralised with acetic acid and filtered from any flocks of silica and alumina that may have separated) in sufficient quantity, and finally acetic acid, till any flocculent precipitate that may have formed from excess of potash has redissolved, and the fluid is decidedly acid. Allow it to stand at least for 24 hours in a warm place, take out a portion of the supernatant fluid with a pipette, mix it with more potassium nitrite, and observe whether a further precipitation takes place in this after long standing. If so, return it to the principal solution, add more potassium nitrite, and repeat the test after long standing. Filter, wash thoroughly with an aqueous solution of neutral potassic acetate (containing 10 per cent. of the salt), and finally with spirit of wine of 80 per cent. Dry, ignite, incinerate the filter, moisten the whole with sulphuric acid, and drive off the excess and weigh. Result, $2\text{CoSO}_4 + 8\text{K}_2\text{SO}_4$.

Separation of Nickel from Iron.

A process proposed in the *Zeitschrift für Anal. Chemie* for separating nickel and iron depends on the insolubility of ferric phosphate in acetic acid, in presence of sodium phosphate in excess, whilst nickel phosphate is soluble. The hot solution of the two metals containing free acetic acid is mixed with sodium phosphate, the ferric precipitate is removed by filtration; from the filtrate nickel phosphate is thrown down by the addition of potash, the precipitate is dissolved in sulphuric acid, the solution is rendered alkaline, and the nickel precipitated by the galvanic current. The process is only applicable where the nickel does not exceed 3 per cent.

Mr. Thomas, F.C.S., for separating nickel from ores containing much iron, adopts the following method:—The ore is dissolved in aqua

regia, the silica separated; to the filtrate ammonia is added in excess, the precipitate of iron oxide well stirred, filtered, and washed with ammoniacal water, the iron redissolved with hydrochloric acid, reprecipitated with excess of ammonia, and treated as before. The two solutions are added together, and boiled to expel excess of ammonia; solution of potassium hydrate is then added, and the solution heated till ammonia is no longer given off, the solution filtered, the precipitate well washed with hot water, redissolved in acid and reprecipitated by potash, washed, dried, ignited, and weighed in the usual manner. Care must be taken that no copper is present during the operation. By this method better results are obtained than by the usual way.

Separation of Nickel from Zinc.

A dilute solution of the nitrates or sulphates is mixed with ammonia till an alkaline reaction is obtained, and then acidified with pure citric acid. When the solution is perfectly cold sulphuretted hydrogen is introduced till the liquid has a distinct smell, which is generally effected in 5 to 10 minutes. If much zinc is present, sulphuretted hydrogen is introduced for 5 minutes at a time, letting the liquid stand after each introduction, and repeating this till the smell of the gas does not disappear on standing. In this manner we avoid a needlessly long treatment with sulphuretted hydrogen, by which traces of nickel sulphide may be carried down. The precipitate of zinc sulphide is allowed to stand for 24 hours in the cold, and is then weighed as such. The filtrate is evaporated to a small volume, and after supersaturation with ammonia the nickel is thrown down electrolytically. In this operation care must be taken that no sal-ammoniac is present, as it hinders the precipitation of nickel. The solution should be a nitrate.

For the separation of zinc and nickel by means of hydrogen sulphide in presence of acetic acid alone, there are required at common temperatures quantities of acid, so much the greater as the proportion of nickel in solution is greater, and under the influence of a temperature but slightly elevated (40°), even in an open vessel, there is always a precipitation of sulphide. It is sufficient to raise to 70° in an open vessel an acetic solution of nickel acetate, which has been saturated with hydrogen sulphide, letting the liquid cool out of direct contact with the air, so as to avoid a too great loss of sulphuretted hydrogen and the occurrence of oxidation, in order to have all the nickel separated as sulphide, which is entirely deposited in 10 to 12 hours.

The method is at fault only if the liquid contains oxidising agents, such as nitrates, but as under these conditions the nitric acid may be destroyed by boiling with ammonium hydrosulphate, it is sufficient to submit the solution to this treatment, repeatedly if needful, in order to effect a complete precipitation of the nickel as sulphide in presence of free acetic acid.

COBALT.

Metallic Cobalt.

Metallic cobalt is precipitated from the aqueous solutions of its salts by magnesium in exactly the same manner as metallic nickel. The subsequent treatment is identical. After fusion in a lime crucible cobalt is one of the most tenacious of known metals, and when made into wire it supports almost double the weight which would break an iron wire of the same thickness.

Estimation of Cobalt.

Leison's process with oxalic acid and permanganate is equally successful with cobalt as with nickel (page 247). A few modifications are necessary. The solution is precipitated in the usual way by oxalic acid and alcohol, but it is then collected on a sand-filter and digested with dilute sulphuric acid. The solution, which will be very red, must then be mixed with a solution of nickel sulphate until the red colour disappears and a faint smoky hue takes its place; the subsequent titration is performed in the customary manner.

Cobalt cannot be estimated by precipitation as sulphide and calcination, with subsequent addition of ammonium carbonate, in the way described under Nickel. Mr. Forbes, who has experimented on this method, says that the calcined mass, instead of consisting of a mixture of cobalt oxide and disulphide, is quite pink from the presence of cobalt sulphate, which appears most strongly to resist decomposition.

For the qualitative estimation of minimum quantities of cobalt C. H. Wolff recommends the characteristic absorption-spectrum of the blue solution obtained on mixing a neutral alcoholic solution of cobalt chloride or nitrate with an alcoholic solution of ammonium sulphocyanide. In order to apply this process to the detection of cobalt in presence of iron and nickel, H. W. Vogel combines it with C. Zimmerman's method of separation, based on the fact that from a mixed solution, containing nickel, cobalt and ferric sulphocyanides, the iron is thrown down as ferric hydrate by the addition of neutral sodium carbonate. Vogel adds to the solution sodium carbonate till the red colour disappears, filters, and shakes the filtrate in a test-tube with a mixture of equal volumes of amyl alcohol and ether. This mixture takes up the cobalt sulphocyanide, and separates as a blue stratum floating above the watery liquid. If nickel is also present the ethereal liquid is not blue, but green. If the liquid is examined in the spectroscope the presence of cobalt is distinguished by the absorption-band between the solar lines C and D.

Tests for Cobalt.

If to a solution of a cobalt salt in tartaric or citric acid an excess of ammonia is added, the addition of potassium ferricyanide will cause

a very dark red colouration in the solution. Mr. Skey says that the colour thus produced by the ferricyanide is so intense that it will reveal the presence of cobalt in solution when all other tests fail, its delicacy being about four times greater than that of ammonium carbonate. A solution of cobalt prepared as indicated above, so as only to contain $\frac{1}{2000}$ part of cobalt, when placed in a $\frac{3}{4}$ -inch test-tube, is very distinctly coloured by the addition of a soluble ferricyanide, and even when diluted down so as to contain but 1 part of cobalt in 400,000 parts of the liquid, the colouration is still distinctly visible in a bulk of a few ounces.

Another very delicate test is given by Herr Schönn. If a drop of cobalt solution be added to a concentrated solution of sodium sulphocyanide, a blue mass is the result. This mass is composed, either immediately or after evaporation, of acicular blue crystals, probably of cobalt sulphocyanide, which are easily soluble in water and alcohol, but insoluble in carbon disulphide. This reaction may be used as a test for cobalt. A drop of a solution containing 0.0005 part of cobalt produces, with sodium sulphocyanide, only a green colour, at ordinary temperatures; on heating, however, the mass becomes blue. As the cobalt solution should always be concentrated, it is well to evaporate dilute solutions nearly to dryness, then add the reagent, and heat. According to Schönn, neither iron, zinc, manganese, nor nickel interferes with the reaction, provided the solution be perfectly neutral.

For the detection of small quantities of cobalt and nickel simultaneously present, E. Donath and J. Mayrhofer proceed as follows:—The precipitate obtained in a systematic analysis, which may consist of nickel and cobalt sulphides, is dissolved in a minimum of nitric acid, mixed with an excess of soda-lye and a corresponding quantity of solid iodine, and boiled. If little nickel and much cobalt are present the precipitate is brown or brownish-black, granular, and loose. In the opposite case it is either like pure nickelous oxide or of a dirty greyish green. It is filtered, washed with hot water, and introduced into a test-tube by perforating the filter. Here it is shaken up with ammonia and a few drops of ammonium chloride solution and filtered. The filtrate, which can only contain nickel, is mixed with a few drops of ammonium sulphide. An immediate dark-brown colouration, followed by a black precipitate, shows the presence of nickel. The residue upon the filter is several times drenched with ammonia, thoroughly washed with hot water, dissolved in a few drops of hydrochloric acid, and the solution boiled with a fragment of solid potash. After the precipitate has subsided, the blue colour of an alkaline cobaltate is observed, which is soon decomposed, with a deposit of brown cobalt oxide.

Mr. T. Tattersall has found that copper completely prevents the reaction.

F. Reichel recommends to dissolve the mixed precipitate, to throw down both metals with potash-lye, and place the precipitate on a filter.

After the liquid is run off the precipitate, without washing, is introduced into a test-tube; a fragment of caustic potash and very little water are added, and the whole is brought to a boil. The more concentrated the potash solution the easier is the separation. The cobalt dissolves with a blue colour, and even very small quantities may thus be detected. The mixture is immediately filtered through a small asbestos filter, which should be in readiness, washing first with hot concentrated potash-lye and then with water.

Mr. A. H. Allen, F.C.S., shows that either one of the four metals—nickel, cobalt, manganese, or zinc—can be readily distinguished from the others by adding first ammonium chloride and excess of ammonia, and then excess of potassium ferricyanide, when one of the following reactions will take place:—

1. A brown precipitate=manganese.
2. A deep red solution=cobalt.
3. No change in the cold—a copper-red precipitate on boiling=nickel.
4. No change in either hot or cold liquid. Add potassium ferrocyanide, white precipitate=zinc.

Mr. R. H. Davies, F.C.S., recommends the following modification of Mr. Skey's test:—When only the two metals—nickel and cobalt—are present in solution, add ammonia until the precipitated hydrates are redissolved (ammonium chloride does not appear to be essential), then potassium ferricyanide. If the amount of cobalt is large, a reddish-brown precipitate of cobalt ferricyanide will occur. This is soluble in excess of the ferricyanide solution, which must then be added until it has disappeared, and a deep red-brown liquid results. If only an exceedingly small quantity of cobalt be present, no precipitate, but a colouration merely (in itself evidence of this metal), will be observed upon the addition of ferricyanide. Potassium ferrocyanide must now be added, and here, again, a precipitate of nickel ferrocyanide will occur if much nickel salt be present. If the liquid remain clear, add hydrochloric acid drop by drop, noting the effect. A precipitate (yellowish-white) upon the addition of from 6 to 12 drops, while the colour due to cobalt ferricyanide remains unchanged, and the liquid is still strongly alkaline, indicates nickel, whilst if none of this element be present no apparent effect will be produced by the hydrochloric acid until suddenly, on neutralisation, the colour disappears, and a yellowish-white precipitate of cobalt ferrocyanide is thrown down.

For the detection of cobalt and nickel, Dr. G. Papasogli adds to an acid solution of the two metals a slight excess of a solution of potassium hydrate, to precipitate the metals in the state of basic salts. The precipitate is allowed to settle, the alkaline liquid decanted off, and the deposit repeatedly washed to remove the excess of potash. A few drops of ammonium chloride and of ammonia are then added, and it is heated in a slight excess of potassium cyanide.

Care must be taken, as far as possible, not to stir the solution of the double cyanide, to prevent the absorption of atmospheric oxygen. If the double cobalt solution is converted into cobalti-cyanide, the addition of an alkaline polysulphide no longer produces the red colouration mentioned above.

The solution of the cyanides is then divided into two portions. To the first are added a few drops of the ammonium polysulphide, so that it may form a stratum above the cyanide solution. If in the place of contact of the two liquids there is observed a red colouration, this indicates the presence of cobalt. The reaction is independent of the presence of nickel, and is sensitive to the fourth and even the fifth decimal place if the solution is sufficiently concentrated.

In the other portion of the solution is immersed a small slip of zinc; if the liquid contains nickel there will be observed, besides the gaseous envelope, an intense red colouration, which shows itself over the whole surface of the slip, but especially at the lower part. The presence of cobalt does not interfere with this reaction, which is still produced even if the solution containing the cobalt has absorbed oxygen.

If the solution is concentrated the sensitiveness of the reaction extends to the fourth decimal place. The presence of ammoniacal salts in excess retards, or even hinders, the reaction.

The solution of potassium cyanide used should be concentrated, but an excess in quantity should be avoided, especially if the quantity of nickel is small. If an excess of the cyanide is used, then, on immersing the slip of zinc, there occurs suddenly a strong evolution of gas, which disperses the red colouration and makes it difficult to perceive the reaction.

To avoid this inconvenience, the author places in the solution to be examined a slip of platinum, joined at one extremity to a slip of zinc. The greater portion of the gas then envelopes the platinum, and as the red colour forms only around the zinc it is less readily dispersed, and the reaction remains more sensitive.

Separation of Cobalt and Nickel.

The following is a convenient method of detecting cobalt and nickel in ordinary analysis, although the process is not sufficiently accurate for quantitative purposes:—To the slightly acid solution containing the two metals, first an excess of ammonium chloride is added; this causes the cobalt ferricyanide afterwards formed, which otherwise would run through the filter, to fall in a denser state, and also of a much darker colour, often nearly black. Potassium ferricyanide is then added, until the precipitation is complete, and it is afterwards strongly agitated with a considerable excess of ammonia. Upon filtering, the cobalt remains upon the filter, being recognised by the characteristic blue colour of the precipitate, and the nickel is readily detected in the filtrate by means of ammonium sulphide.

A method of separating nickel and cobalt, given some years since by Liebig, consists in boiling the mixed double cyanides of nickel and potassium and cobalt and potassium with mercury oxide. Nickel oxide is precipitated, while an equivalent quantity of mercury is dissolved in the cyanide. The method certainly gives good results, but is not free from objection. Long boiling is necessary before the precipitation is complete, and it is difficult to prevent bumping during ebullition. The excess of mercury oxide must be separated from the nickel oxide by a special operation, and the nickel afterwards again precipitated by caustic alkali.

These inconveniences may be completely avoided, according to Wolcott Gibbs, by employing, instead of the oxide alone, a solution of the oxide in the mercury cyanide. When this solution is added to a hot solution of the nickel and potassium double cyanide, the whole of the nickel is immediately thrown down as a pale green hydrate of the protoxide. Under the same circumstances, cobalt is not precipitated from the double cobalt and potassium cyanide. Mr. W. N. Hill, who has repeatedly employed this method and carefully tested it, has found that the separation effected is complete. No cobalt can be detected in the precipitated nickel oxide by the blowpipe, nor can the nickel be detected in the cobalt (finally separated as oxide) by Plattner's process with the gold bead. The solution of mercury oxide is easily obtained by boiling the oxide with a strong solution of the cyanide, and filtering. The hydrated nickel oxide precipitated may be filtered off, washed, dried, ignited, and weighed. The cobalt is more readily and conveniently estimated by difference when the two metals have been weighed together as sulphides.

Mr. T. H. Henry has mentioned another objection to Liebig's process referred to above. The potassium cyanide employed should be free from cyanate, and as the commercial salt always contains cyanate, Liebig proposed instead the employment of hydrocyanic acid and caustic potash. Mr. Henry fuses commercial potassium cyanide, for a few minutes, with a little pure charcoal, and, when cold, dissolves it in water and uses this solution instead of the pure salt or the mixture of hydrocyanic acid and potash. The rest of the operation may be carried out as directed by Liebig (boiling the solution with mercury oxide), or by Dr. Gibbs's modification, as described in the preceding paragraph. Mr. Henry says that he believes this process to be one of the most elegant, accurate, and expeditious in the whole range of analytical chemistry.

Dr. Phipson gives the following method of isolating minute quantities of nickel in cobalt chloride:—A few grains of that salt are dissolved in water, and the whole of the cobalt precipitated, with the nickel, by potassium xanthate employed in slight excess, and previously dissolved in a little distilled water. A few drops of ammonia are then added, just sufficient to render the liquid slightly alkaline, and

the dark green cobalt xanthate is collected on a filter. The whole of the nickel is in the filtrate, and the whole of the cobalt in the filter. The nickel in the filtrate is precipitated by a few drops of ammonium sulphide.

Dr. A. Jorissen gives the following method for the same purpose. The action of reducing agents upon nickel hydroxide is much more energetic than upon cobalt hydroxide. The difference in the behaviour of the two oxides can be advantageously used for the detection and separation of nickel in presence of much cobalt. The two hydroxides are precipitated by the successive application of soda-lye, and of a quantity of bromine sufficient to convert all the nickel and cobalt into oxide. 1 or 2 c.c. of solution of potassium cyanide are then added, without previous filtration, and the mixture is well shaken in the cold. It is then filtered, and the filtrate, after addition of aqua regia, is evaporated to dryness. On redissolving the residue in water, there is obtained a solution of nickelous chloride, which shows the characteristic reactions of nickel very distinctly. The successive application of ammonia and ammonium sulphide is particularly recommended, which gives a dark brown liquid. Or the solution may be treated first with soda-lye and then with bromine. When the black precipitate has thus been formed, 2 or 3 drops of potassium cyanide are added. The precipitate disappears very quickly in the cold, and a clear solution remains. It must be noted that if a solution of very much nickel and little cobalt is treated in the manner above described, the latter enters into solution.

If two solutions of equal quantities of cobalt are submitted to the above-described process, the one containing in addition a tenfold proportion of nickel, and if in each case there is added an equal number of c.c. of solution of potassium cyanide, it will be observed that the solution containing nickel and cobalt is almost entirely decolourised, whilst the other still contains black flocks in suspension. If a small quantity of potassium cyanide is used, it is always possible to separate a quantity of nickel sufficient for recognition.

G. Delvaux separates the two metals, by two known methods permitting the exact estimation of the two oxides, and the preparation of the two metals in a state of purity. The two fundamental processes are that of Pisani, who uses caustic potash in presence of an ammoniacal liquid, in which are dissolved the two metals, with exclusion of air. The nickel oxide is precipitated alone in bulk, but always carries down with it more or less of cobalt oxide. The second method is that of Terreil, who precipitates cobalt in an acid solution in a state of roseo-cobaltic hydrochlorate. The cobalt oxide is peroxidised by means of permanganate. We suppose that the two bodies, cobalt and nickel, have been obtained by known methods, either as pure oxides or pure sulphides, free from all foreign matter. The mixed oxides or sulphides are dissolved in an aqua regia containing a large proportion of hydro-

chloric acid. The solution is largely diluted with water and saturated with ammonia in excess. Permanganate is then added until the solution remains rose-coloured for some time. Pure potash is then added, when the nickel is precipitated as hydroxide, carrying with it manganese oxide, derived from the permanganate. The precipitate is washed by decantation and filtered; redissolved in hydrochloric acid, and treated again with ammonia, permanganate, and caustic potash. The washing-waters which contain the cobalt are collected, saturated with acetic acid, and precipitated by sulphuretted hydrogen. The mixture of nickel and manganese oxides is redissolved in hydrochloric acid, and the solution saturated with ammonia. The solution is exposed to the air for some time, and the manganese oxide is by degrees entirely precipitated. It is filtered off, the filtrate is saturated with acetic acid, and the nickel thrown down by means of sulphuretted hydrogen. The process may be employed on the large scale for obtaining nickel completely free from cobalt.

M. P. Dirvell finds a method on the following facts:—

1. If there be added to the aqueous solution of cobalt nitrate or sulphate an excess of cold saturated solution of phosphorus salt, mixed with a solution of ammonium bicarbonate from which no ammoniacal odour is emitted, a bluish precipitate is formed in the liquid. When the mixture is slowly warmed the equivalent of carbonic acid in excess at first escapes; then by boiling for a few seconds, a very distinct ammoniacal odour is perceptible. At this moment the boiling is discontinued, and from 2 to 3 c.c. of ammonia added to the liquid. The precipitate is for the most part dissolved, and it is only necessary to warm gently to 100° to obtain a precipitate of a beautiful purple, inclining to violet, which is rapidly deposited. It loses no ammonia at 100° , and is transformed at a red heat into pyrophosphate.

2. A solution of the corresponding nickel salts treated in the same manner gives only a pure blue liquid, which is not rendered turbid by heat.

8. By mixing the two above-mentioned reagents in excess with a solution containing cobalt and nickel, and treating in the same manner, the red precipitate of ammonio-cobaltic phosphate is again obtained, whilst the remaining blue liquor contains the whole of the nickel. By this means the cobalt in the nickel sulphate of commerce can be detected.

It is better to make this separation for the qualitative research of the two metals in assay-flasks, when evaporation is slow. For the quantitative separation prepare the reagents in the following manner:—1.8 gramme of phosphorus salt is digested in the cold in 250 grammes of water; 2.3 grammes of effloresced ammonium carbonate are dissolved in the same quantity of water, and the solution saturated with carbonic acid till all ammoniacal smell is gone.

After having separated the two oxides in the customary way, and

having reduced them by hydrogen, they are weighed, dissolved in nitric acid, and the acid solution evaporated to dryness in a water-bath. The residue is redissolved in about 50 c.c. of water, to which is added a quantity of phosphorus salt equal to 30 times the weight of the two metals, and to which a volume of ammonium bicarbonate equal to that occupied by the phosphate has previously been added. Then operate as has already been indicated, care being taken to frequently shake the flask containing the liquid, especially after the addition of the ammonia.

If the boiling has inadvertently been too prolonged, causing the evaporation of the blue liquid containing the nickel on the sides of the vessel, and the consequent precipitation of a little nickel, it is easily ascertained by the colour of the cobalt precipitate, which will, in this case, be paler. It can also be compared with the moist ammonio-cobaltic phosphate, which is kept in a bottle to act as a test. In this case the clear blue liquor is drawn off, the red precipitate dissolved in only as much dilute phosphoric acid as is absolutely necessary (it is even better to leave a little precipitate undissolved), then the operation is continued with ammonium bicarbonate and ammonia.

In all cases the precipitate is washed in cold water, weighed on a tared filter at 100°, or calcined; 100 parts of the calcined precipitate contain 40.4 of cobalt. With regard to the blue liquid separated by filtration, sulphuretted hydrogen completely precipitates the nickel. The precipitate is calcined in a crucible with some sulphur and weighed in the state of sulphide.

This method is an exceedingly rapid one, for the separation requires only 1 or 2 hours at the most.

Dr. Wolcott Gibbs gives the following method for the estimation of cobalt. The extraordinary stability of the potassium cobalt-cyanide enables us to separate cobalt advantageously from many other metals by bringing it into this form. Wöhler first proposed to precipitate the double cyanide by mercurous nitrate, and to weigh the cobalt finally as metal. It is particularly advantageous to precipitate at a boiling heat, and then boil for a few minutes with mercuric oxide, so as to neutralise as completely as possible any traces of free nitric acid. By precipitating from hot solutions a granular, crystalline mercurous salt is obtained, which is very readily washed.

E. Donath has adapted a modification of Fleischer's process which depends upon the following facts: If a cobalt solution is mixed with excess of potash- or soda-lye, and brought to a boil, the cobalt hydroxide is as completely converted into sesquioxide as by treatment with bromine. Nickel oxide is not affected by this process. Hence in the one half of the solution of the mixed metals both are converted into sesquioxides by boiling with alkali and bromine, whilst in the other half merely the cobalt is converted into sesquioxide by a similar treatment with alkali and iodine.

The precipitate, freshly taken from the filter, is boiled with hydrochloric acid in a suitable distilling apparatus, and the chlorine evolved is collected in solution of potassium iodide, and the iodine separated is estimated volumetrically by a decinormal solution of sodium dithionate.

As one atom of iodine corresponds to an atom of cobalt or nickel, and the atomic weights of the two latter are equal to 59, the difference of the required number c.c. of the dithionate solution in both estimations, multiplied by 0.0059, represents the weight of the nickel; the number in the second case, where only the cobalt is converted into sesquioxide, if multiplied by 0.0059, gives the weight of the cobalt. In this modification of Fleischer's process the cobalt admits of direct volumetric estimation in a single operation. In the estimation of both metals, the treatment with boiling ammonia is dispensed with, and certainty is reached that the nickel is present in the precipitate merely as nickel oxide.

In converting the cobalt into sesquioxide by treatment with iodine in an alkaline solution, the iodine is added at common temperatures, so long as the colour of the precipitate grows darker; the liquid is then raised to a boil.

If the nickel predominates in quantity, the solutions of both metals are used in a dilute state, otherwise the conversion of the cobalt into sesquioxide may be delayed by a coating of nickel oxide.

M. A. Guyard separates, in the usual manner, the cobalt and nickel from the metals which accompany them; then precipitates both by a slight excess of ammonium sulphide. Dilute the liquid with a suitable quantity of water; then add gradually a weak solution of potassium cyanide, avoiding excess. This operation is rendered easy by the fact that the mass of sulphides clears up, and the cobalt sulphide floats in particles detached from each other, and we distinctly see what passes in the liquid. Then filter, collect the cobalt sulphide, and estimate the cobalt in the ordinary way. To isolate the nickel, acidulate the filtered liquid with a slight excess of hydrochloric or sulphuric acid. The nickel is precipitated in the state of cyanide, and that so completely that we cannot find traces of it in the liquid. This cyanide is collected upon a filter, well washed, and then calcined. Nickel oxide is thus obtained so pure, in some cases that it may be weighed and estimated at once as nickel. However, in general, it is prudent to purify this oxide, which often retains silica; in this case proceed in the ordinary manner.

The advantage of this process for the separation of nickel and cobalt is, that it permits us to estimate the nickel without having to manipulate it in the state of sulphide—an operation always long, very delicate, and very troublesome.

Under favourable circumstances the analytic process just explained is very simple, and may be applied to the separation of nickel and cobalt on a large scale.

Separation of Nickel and Cobalt from their Ores and from one another.

As the constituents of a cobalt or nickel ore may be of the most varied description, it is necessary, before attempting to effect a complete separation and estimation of these two metals, either to begin with a careful qualitative analysis, and then to select methods for the separation of each foreign constituent, which would often involve a number of distinct troublesome processes not fitting conveniently one into the other, or else to be in possession of a method so generally applicable as to be capable of effectually eliminating nickel and cobalt from all other elements; and at the same time so simple that even if certain elements, which it is especially designed to separate, should happen not to be present, it would cause no unnecessary waste of time. Mr. E. Ash Hadow has devised an analytical process which is generally applicable to all descriptions of ores of these metals, and he has also suggested a method by which the cobalt usually contained in the manganese ores may easily and profitably be rescued from the waste manganese solutions of the bleaching powder works.

The following is condensed from Mr. Hadow's original paper, which will be found in the *Chemical News*, vol. ii. p. 85:—If no qualitative analysis of the ore has been previously made, we must presume, in the quantitative separation of cobalt and nickel, that all other common elements are present; attention, however, need only be specially given to those elements, or their compounds, of which the separation is particularly difficult; these are iron, manganese, zinc, aluminium, magnesium, calcium, arsenic, soluble silica, and phosphoric acid. By employing, however, the method usually applied to the separation of phosphoric acid for the removal of iron, arsenic, and aluminium, and one of the methods recommended for the separation of manganese from cobalt, for the removal likewise of magnesium, calcium, soluble silica, and the last traces of aluminium, and by a slight modification for the detection and separation of zinc, the analysis becomes short, easy, and accurate.

The only examination which the ore need undergo previously to the solution of a weighed quantity, is with the view of obtaining a rough idea as to the amount of arsenic and cobalt or nickel present in the sample; for this purpose a little may be roasted on charcoal, or ignited in a tube, to see whether arsenic readily sublimes; another portion, of a few grains weight, may be dissolved in aqua regia in a test-tube, when the depth of the blue or green colour will serve as an indication of the degree of richness of the ore in cobalt and nickel.

If the ore is rich, from 20 to 80 grains; if poor, from 50 to 100 grains, in a state of fine division, are weighed out for the analysis. If much arsenic has been found, the portion, after weighing, had better be ignited in a small porcelain capsule or crucible over a gauze burner,

when it generally ignites and smoulders away, evolving abundance of arsenious acid. The powder ready for solution is transferred to a small 4-ounce flask by means of glazed letter-paper and a camel's-hair paint brush to sweep in the last particles; the mouth of the flask is then partially closed by a small funnel placed to catch the drops projected during solution. The ore is then drenched with hydrochloric acid, nitric acid being added from time to time, until all heavy metallic-looking particles are found to have disappeared from the bottom of the flask. The solution may then be decanted from the insoluble matters into a half-pint beaker, together with the washings of the flask; and as sulphur frequently remains, entangling portions of undissolved ore, it is advisable to transfer the undissolved residue from the flask into a capsule, drying and igniting the contents of the latter, and then digesting again the ignited matters in a little more aqua regia; the whole of the latter, both dissolved and undissolved, may now be added to the first portion in the half-pint beaker.

To separate out iron, arsenic, phosphoric acid, and aluminium from the solution, sodium acetate may be added at once, and the liquid boiled; a far better mode, however, is to effect a *partial* separation of these ingredients by the addition of calcium carbonate in excess to the solution of the ore, and after filtering the solution containing the greater portion of the cobalt and nickel, and partly washing the precipitate, to extract the last traces of cobalt and nickel from the latter by dissolving it in hydrochloric acid, adding excess of sodium acetate, and boiling. The first filtrate from the precipitate by calcium carbonate had better be collected apart from the second filtrate from the precipitate produced by sodium acetate, and received in a beaker capable of holding at least a quart. The solution of the precipitate by calcium carbonate is best effected in a beaker, after the removal of the precipitate from the filter; this is easily effected by inclining the funnel over the beaker and sending a stream of water from the wash-bottle between the filter and the upper edge of the mass of precipitate, when the latter will soon become detached and slide off into the beaker below; it is here treated with dilute hydrochloric acid, to dissolve all but the insoluble residues of the ore which had not been previously filtered off, and then a solution of sodium acetate is added in excess (indicated by the deep red colour of liquid), and the whole, heated to boiling, may be filtered at once. Iron thus separated out, in presence of free acetic acid, has less tendency to retain cobalt than when precipitated by means of calcium carbonate, besides which the cobalt and nickel in the filtrate are left in the condition of acetates, a necessary step preparatory to their separation from manganese, &c.

This method of separating out iron, &c., though very effectual, was often at first found to be attended with difficulties, for if much arsenic were not present the basic iron acetate frequently became slimy towards the end of the filtration, only allowing the boiling wash-water to

pass with such extreme slowness as to render the method almost useless, until it was found that the addition of a little sodium sulphate during the washing at once and permanently effected a cure, causing filtration to proceed rapidly, and diminishing the tendency of the iron to pass the filter; another difficulty was, that when sodium acetate was added at once to the original solution of the ore, the solution, often containing much cobalt and nickel as acetates, and filtered in a concentrated state, yielded to the filter paper sufficient cobalt and nickel to occasion distinct loss; this was avoided by separating out the great bulk of the cobalt and nickel in solution as chlorides by means of calcium carbonate, as above recommended, and then the weaker solution, being comparatively strongly acid, could be filtered without loss. This second filtrate may still retain traces of iron; a little sodium acetate may be added to make sure that none remains in the condition of chloride, which would be indicated at once by a reddening of the liquid, and the whole is then boiled thoroughly once more; if rendered at all turbid, passed through a filter again, then nearly neutralised with ammonia, and finally added to the bulk of the cobalt and nickel solution in the quart beaker. There will in all probability be enough of the sodium and ammonium acetates present to convert the entire quantity of cobalt and nickel into acetates without further addition, and rendering it thus ready for the next operation.

If sulphuretted hydrogen be now passed through the solution containing cobalt and nickel, these metals are perfectly and completely separated without a trace of manganese, magnesium, calcium, aluminium, or soluble silica, which, when present, invariably accompany the sulphides precipitated by ammonium sulphide; the sulphides, moreover, thus precipitated from an acetic solution, have much less tendency to oxidise while on the filter, so that their washing may be more perfectly accomplished than in the former case. The passage of sulphuretted hydrogen may be conveniently effected at the end of the day, and the next morning the sulphides will be found perfectly settled at the bottom of the beaker, permitting the great bulk of the liquid (tested first to make sure of the removal of cobalt and nickel) to be drawn off and thrown away, or at least rapidly run through a filter; the sulphides collected at the bottom, together with that which always adheres to the sides of the beaker, and which may be detached without loss by a caoutchouc-covered glass rod, are then well washed on the filter with boiling water until all soluble matters are perfectly removed. The sulphides, perfectly washed, are now to be dried by placing the funnel with the filter in a broken beaker on wire gauze, at a safe distance over a lamp, and when dry they may be detached from the filter into a small beaker of from 1 to 2 ounce capacity, capable of being covered with a watch-glass; the filter itself is ignited, and the well-burnt ashes added to the sulphides, which are then to be *cautiously* treated with nitric acid, the action being rather violent, and, if care

be not taken, liable to occasion loss. With the aid of a little heat the whole should pass into solution.

In addition to cobalt and nickel the solution may still contain zinc, together with copper, and other metals precipitable by sulphuretted hydrogen from hydrochloric solutions; by passing sulphuretted hydrogen now through the nitric solution, somewhat diluted, these latter are readily precipitated and removed by filtration. Zinc, however, may still remain, to detect and remove which it is necessary to expel the sulphuretted hydrogen still remaining in the solution by boiling, to add solution of ammonia until a precipitate occurs, and then to acidify pretty strongly with acetic acid; if sulphuretted hydrogen slowly transmitted, or fresh sulphuretted hydrogen water, occasions a milkiness, zinc is present, and the slow passage of the gas is to be continued until the precipitate begins to show signs of darkening. The liquid is then filtered. The zinc may be identified as such by collecting and igniting the precipitate, when a trace of cobalt carried down with it (and which may be separated out, if desired, by a repetition of the process on the precipitate) will produce the beautiful and well-known Rinman's green.

The filtrate, containing only nickel, cobalt, and ammonium salts, is treated with some pure sulphuric acid and evaporated to dryness in a weighed capsule, and heated sufficiently to expel the excess of sulphuric acid and all the ammoniacal salts. The residual cobalt and nickel sulphates may now be weighed in a covered crucible. This form of weighing these metals is easy, exact, and may be rapidly executed. The weight of the ash of a filter of the size used for collecting the sulphides must be ascertained after treatment with sulphuric acid, and subsequent expulsion of the excess, and this weight deducted from the total sulphates, in order to obtain perfectly correct results.

If it be desired to weigh these metals as oxides, pure potash or sodium carbonate must be substituted for ammonia, with acetic acid for the removal of zinc, and after the precipitation of the latter the filtrate must be first acidified with hydrochloric acid and boiled to expel sulphuretted hydrogen, and finally supersaturated with potash; the precipitate thus obtained is, however, difficult to wash, and almost always contains some silica derived from the potash or the vessel in which the operation was conducted, and is not to be recommended as so convenient or exact a form as that of the sulphate. After ignition of the oxides, the nickel exists as NiO , and the cobalt as Co_3O_4 .

Potassium binoxalate serves as a perfect precipitant of nickel, but cobalt is not so thoroughly separated; the first goes down as a nickel and potassium double salt, the latter as a simple oxalate; both precipitates are very easily washed, and give perfectly correct results with nickel, nearly correct with cobalt; the former precipitate must, after ignition in an open crucible, be washed with a little water to remove

the potassium carbonate, and again dried and weighed as oxide, NiO ; the cobalt oxalate strongly ignited in the open air leaves the oxide Co_2O_3 .

It now only remains to separate the nickel and cobalt from each other. If the colour of the solution indicates that the latter is in excess, Liebig's method of separation by converting the metals into double cyanides is probably preferable to any other; perfectly correct results are, however, only attained when certain precautions are taken; in the first place, it is not altogether a matter of indifference whether the mixed sulphates or the oxides brought into solution in hydrochloric acid be treated with potash or with hydrocyanic acid first, unless, indeed, the potash be perfectly free from silica; if the latter be present, and the potash is added first, the precipitate produced frequently refuses wholly to dissolve on the addition of hydrocyanic acid, and though liable to be disregarded from making little show in the coloured liquid, it will, if filtered off, be found to retain cobalt. Therefore, hydrocyanic acid should always be added first, and the subsequent addition of potash will then produce perfect solution, even though silica should be abundantly present in the potash; a condition which is, however, to be avoided, as the silica will afterwards attach itself to the nickel precipitate. The most important point to be attended to is the complete conversion of the cobaltous- into the cobalti-cyanide, a change which is effected by the absorption of oxygen from the air; this takes place with great rapidity, but still not so rapidly but that, by the hasty addition of mercury oxide, a considerable quantity of cobalt might be precipitated with the nickel. The change from the absorption of oxygen is easily seen if the solution is cold, by the liquid, at first of a deep yellowish-green, becoming rapidly, from the surface downwards, of a deep reddish-brown, which changes to pale yellow when warmed. There is no need of *free* hydrocyanic acid, neither can any hydrogen be observed to escape on boiling the solution of a cobaltous-cyanide. When the change from cobaltous- into cobalti-cyanide is complete (which may be ascertained by withdrawing the source of heat and observing whether the cooling liquid continues to remain of a pale yellow colour) the nickel may be precipitated either as pale hydrated protoxide, by the addition of precipitated mercury oxide, or as the black hydrated sesquioxide, by means of chlorine or sodium hypochlorite.

The latter appears to be the best of the two methods, for the following reasons:—1st. That it serves as a qualitative test in the first instance for the presence of nickel, the *least trace* of the sesquioxide giving an inkiness to the liquid, whereas, when mercury oxide is used, the excess of mercury oxide completely disguises a small quantity of the pale green nickel protoxide, which can only be detected after washing and igniting the precipitate. 2nd. The hydrated protoxide, separated by mercury oxide, may easily carry down some cobalt as nickel cobalti-cyanide unless the liquid is strongly alkaline; this is not the

case with the sesquioxide, even when precipitated from liquids nearly neutral. 3rd. The first action of the chlorine, or sodium hypochlorite, is upon the cobaltous cyanide, effectually ensuring its conversion into cobalti-cyanide, before the nickel cyanide is touched. 4th. The nickel sesquioxide is washed with far greater ease and rapidity than the protoxide. If potash is used it must be pure and free from silica and aluminium, hence, for the sake of economy, sodium carbonate may be substituted for it, the carbonic acid escaping with effervescence on the passage of chlorine into the boiling liquid. A more convenient way, perhaps, is to add to the boiling solution of the cyanides a previously prepared solution of sodium hypochlorite containing excess of sodium carbonate, as long as it continues to produce a precipitate.

If the separation of nickel by mercury oxide be preferred, a solution of a mercury salt may be substituted for the previously prepared oxide with advantage as regards economy, rapidity, and neatness; the excess of alkali in the liquid produces a momentary precipitation of mercury oxide with each drop added, until the nickelous-cyanide has been wholly decomposed, when the yellow colour of the mercury oxide appears permanently.

If it be desired to weigh the cobalt of the cobalti-cyanide, after the separation of the nickel by Wöhler's method of precipitating the solution with nitrate of the mercury suboxide, chlorides and sulphates are to be avoided as giving rise to very bulky precipitates; and accordingly, after the separation of zinc, the nickel and cobalt should be precipitated by potash, brought into solution in nitric acid, and after conversion into cyanides, nitrate of mercury protoxide may be used to separate out nickel. In washing the mercurous cobalti-cyanide, its disagreeable tendency to pass through the filter towards the conclusion of the washing may be effectually prevented by adding a little nitrate of mercury suboxide to the washing water.

If the colour of the solution of the mixed oxides indicates that nickel is decidedly in excess, it will be better, before proceeding to separate out the cobalt by Liebig's method, to concentrate the cobalt by a previous partial separation by a method which Mr. Merry, of Swansea, employs to effect a complete and entire separation of the two metals. It is a modification of Rose's method for their separation, and consists in adding to the perfectly neutral solutions of the two, a solution of calcium hypochlorite as long as it produces an immediate black precipitate of cobalt sesquioxide. To extract the last traces of cobalt the addition of calcium hypochlorite must be carried somewhat beyond this, since a black precipitate forming even after some minutes often contains a trace of cobalt; if there be much of the latter the liquid must be neutralised from time to time with lime-water or milk of lime. The black precipitate, containing all the cobalt with some nickel, can then be brought into solution, and the cobalt separated out either by Liebig's method or by a repetition of the above process.

This method is a very useful one for detecting the smallest trace of cobalt in a solution of nickel :—The solution digested in the cold on lime carbonate, to render it neutral, is filtered and treated with a few drops of a solution of calcium hypochlorite ; if cobalt is present to a certain extent an immediate brown cloud is perceived, but if far less than this the dark precipitate which will form after some time will certainly contain cobalt, if any be present, and on dissolving in borax will become manifest, if not at once, at least when the nickel has been reduced by ignition on charcoal before the blowpipe, by the blue colour of the bead.

The property which cobalt possesses of being perfectly precipitated from its acetic solution by sulphuretted hydrogen, and thus of being separated from manganese, might probably be profitably employed to recover the cobalt which is contained in the solutions of manganese from the bleaching-powder works. All that is necessary is to add to the liquid an excess of chalk, which would remove all the iron and render the liquid neutral ; the latter drawn off from the precipitate would merely require the addition of a very little sodium acetate, about 90 parts of the dried salt to every 40 of the commercial cobalt oxide in the liquid (which would have to be estimated by a separate examination of a portion), and then sulphuretted hydrogen transmitted would precipitate all the cobalt as sulphide at once.

In the analysis of nickel and cobalt ores and furnace products, Professor R. Fresenius proceeds as follows :—The material in fine powder is treated with hydrochloric acid, mixed with nitric acid, till everything soluble is dissolved. It is then repeatedly evaporated almost to dryness with hydrochloric acid to expel the rest of the nitric acid. The residue is taken up with dilute hydrochloric acid and filtered. If the residue left is not perfectly white it is fused with potassium bisulphate, the melted mass treated with hydrochloric acid and water, the solution filtered and added to the former. A current of hydrogen sulphide is passed through the liquid, which contains a sufficiency of hydrochloric acid, so as to throw down all precipitable metals. The gas is passed in first at 70° C., and afterwards in the cold. The filtrate is heated first alone and then with the gradual addition of nitric acid to convert ferrous oxide into ferric. Ammonia is then added in excess ; the impure hydrated iron oxide filtered off, washed a little, dissolved in hydrochloric acid ; the solution, considerably diluted, mixed with sal-ammoniac, and then, in the cold, with a dilute solution of ammonium carbonate, until the liquid takes a somewhat turbid appearance, without, however, the formation of a precipitate. On standing it should not become bright, but of the two rather more turbid. The reaction of the liquid is still decidedly acid. It is now heated to a boil, the precipitate of basic ferric salt is washed with boiling water, first by decantation and then upon the filter, and a portion of the basic salt is then tested by dissolving in hydrochloric

case with the sesquioxide, even when precipitated from liquids nearly neutral. 3rd. The first action of the chlorine, or sodium hypochlorite, is upon the cobaltous cyanide, effectually ensuring its conversion into cobalti-cyanide, before the nickel cyanide is touched. 4th. The nickel sesquioxide is washed with far greater ease and rapidity than the protoxide. If potash is used it must be pure and free from silica and aluminium, hence, for the sake of economy, sodium carbonate may be substituted for it, the carbonic acid escaping with effervescence on the passage of chlorine into the boiling liquid. A more convenient way, perhaps, is to add to the boiling solution of the cyanides a previously prepared solution of sodium hypochlorite containing excess of sodium carbonate, as long as it continues to produce a precipitate.

If the separation of nickel by mercury oxide be preferred, a solution of a mercury salt may be substituted for the previously prepared oxide with advantage as regards economy, rapidity, and neatness; the excess of alkali in the liquid produces a momentary precipitation of mercury oxide with each drop added, until the nickelous-cyanide has been wholly decomposed, when the yellow colour of the mercury oxide appears permanently.

If it be desired to weigh the cobalt of the cobalti-cyanide, after the separation of the nickel by Wöhler's method of precipitating the solution with nitrate of the mercury suboxide, chlorides and sulphates are to be avoided as giving rise to very bulky precipitates; and accordingly, after the separation of zinc, the nickel and cobalt should be precipitated by potash, brought into solution in nitric acid, and after conversion into cyanides, nitrate of mercury protoxide may be used to separate out nickel. In washing the mercurous cobalti-cyanide, its disagreeable tendency to pass through the filter towards the conclusion of the washing may be effectually prevented by adding a little nitrate of mercury suboxide to the washing water.

If the colour of the solution of the mixed oxides indicates that nickel is decidedly in excess, it will be better, before proceeding to separate out the cobalt by Liebig's method, to concentrate the cobalt by a previous partial separation by a method which Mr. Merry, of Swansea, employs to effect a complete and entire separation of the two metals. It is a modification of Rose's method for their separation, and consists in adding to the perfectly neutral solutions of the two, a solution of calcium hypochlorite as long as it produces an immediate black precipitate of cobalt sesquioxide. To extract the last traces of cobalt the addition of calcium hypochlorite must be carried somewhat beyond this, since a black precipitate forming even after some minutes often contains a trace of cobalt; if there be much of the latter the liquid must be neutralised from time to time with lime-water or milk of lime. The black precipitate, containing all the cobalt with some nickel, can then be brought into solution, and the cobalt separated out either by Liebig's method or by a repetition of the above process.

This method is a very useful one for detecting the smallest trace of cobalt in a solution of nickel :—The solution digested in the cold on lime carbonate, to render it neutral, is filtered and treated with a few drops of a solution of calcium hypochlorite ; if cobalt is present to a certain extent an immediate brown cloud is perceived, but if far less than this the dark precipitate which will form after some time will certainly contain cobalt, if any be present, and on dissolving in borax will become manifest, if not at once, at least when the nickel has been reduced by ignition on charcoal before the blowpipe, by the blue colour of the bead.

The property which cobalt possesses of being perfectly precipitated from its acetic solution by sulphuretted hydrogen, and thus of being separated from manganese, might probably be profitably employed to recover the cobalt which is contained in the solutions of manganese from the bleaching-powder works. All that is necessary is to add to the liquid an excess of chalk, which would remove all the iron and render the liquid neutral ; the latter drawn off from the precipitate would merely require the addition of a very little sodium acetate, about 90 parts of the dried salt to every 40 of the commercial cobalt oxide in the liquid (which would have to be estimated by a separate examination of a portion), and then sulphuretted hydrogen transmitted would precipitate all the cobalt as sulphide at once.

In the analysis of nickel and cobalt ores and furnace products, Professor R. Fresenius proceeds as follows :—The material in fine powder is treated with hydrochloric acid, mixed with nitric acid, till everything soluble is dissolved. It is then repeatedly evaporated almost to dryness with hydrochloric acid to expel the rest of the nitric acid. The residue is taken up with dilute hydrochloric acid and filtered. If the residue left is not perfectly white it is fused with potassium bisulphate, the melted mass treated with hydrochloric acid and water, the solution filtered and added to the former. A current of hydrogen sulphide is passed through the liquid, which contains a sufficiency of hydrochloric acid, so as to throw down all precipitable metals. The gas is passed in first at 70° C., and afterwards in the cold. The filtrate is heated first alone and then with the gradual addition of nitric acid to convert ferrous oxide into ferric. Ammonia is then added in excess ; the impure hydrated iron oxide filtered off, washed a little, dissolved in hydrochloric acid ; the solution, considerably diluted, mixed with sal-ammoniac, and then, in the cold, with a dilute solution of ammonium carbonate, until the liquid takes a somewhat turbid appearance, without, however, the formation of a precipitate. On standing it should not become bright, but of the two rather more turbid. The reaction of the liquid is still decidedly acid. It is now heated to a boil, the precipitate of basic ferric salt is washed with boiling water, first by decantation and then upon the filter, and a portion of the basic salt is then tested by dissolving in hydrochloric

acid, repeating the basic precipitation and testing the filtrate with ammonium sulphide for traces of nickel. If nickel is found the entire precipitate is dissolved in hydrochloric acid, and the iron oxide once more separated as a basic salt in the same manner. The 2 or 3 filtrates, as the case may be, containing the nickel and cobalt are mixed together, acidulated with acetic acid, and concentrated by evaporation. If a slight precipitate appears (ferric oxide or alumina) it is filtered off, redissolved in hydrochloric acid, the solution precipitated with ammonia in excess, and the operation again repeated. The filtered and sufficiently concentrated solution, containing all the nickel and cobalt, is now mixed with sodium carbonate till distinctly alkaline, and acetic acid is then added till it predominates. To the clear liquid are added 20 to 50 c.c. of a solution of sodium acetate containing $\frac{1}{10}$ its weight of the dry salt, and hydrogen sulphide is passed into the liquid at 70° C. When the precipitation is complete, the sediment of cobalt and nickel sulphides is filtered off and dried. The filtrate is concentrated, ammonium sulphide containing an excess of hydrogen sulphide is added, and afterwards acetic acid, and thus a second precipitate of cobalt and nickel sulphides is often obtained. For safety's sake the filtrate is tested once more, to be certain that all nickel and cobalt have been thrown down as sulphides. The dried sulphides, together with the ash of the filter, are now treated with hydrochloric acid, with the addition of nitric acid, until completely decomposed and dissolved. The solution is evaporated with hydrochloric acid to expel nitric acid, diluted with water, filtered, and the solution precipitated with pure potash-lye, preferably in a large platinum capsule. The precipitate obtained is thoroughly washed with boiling water, first by decantation and then on the filter. It is then heated in a Rose's crucible in a stream of pure hydrogen till the weight is constant. The metallic cobalt and nickel are treated in the crucible with boiling water. If the liquid shows an alkaline reaction, or contains chlorine and sulphuric acid, or leaves a residue when evaporated on platinum foil, the metals are exhausted with boiling water, again ignited in a stream of hydrogen, and weighed. The metals are now dissolved in nitric acid, whereby generally a small quantity of silica remains undissolved. It is collected upon a small filter and its weight determined. The nitric acid solution is almost neutralised with ammonia, ammonium carbonate is added in excess, and the whole gently heated for some time. The slight precipitate of alumina and ferric hydroxide which is usually formed is filtered off, dissolved in hydrochloric acid, and re-precipitated with ammonium carbonate. The small precipitate is ignited, first in the air, then in a stream of hydrogen, and its weight, together with that of the silicic acid, is deducted from the gross weight of the metals. If the ores, &c. contain zinc, the mixture of nickel and cobalt obtained as above contains zinc. In this case the hydrochloric solution obtained by dissolving the cobalt and nickel sulphides, after it has been concen-

trated to a small volume, is mixed with pure ammonium chloride in small crystals, to such an extent that 5 parts ammonium chloride are allotted to 0.2 zinc oxide. The moist saline mass is evaporated to dryness and carefully heated till all the sal-ammoniac, and with it all the zinc, is volatilised. The residue of metallic nickel and cobalt is dissolved in hydrochloric acid, with the addition of nitric acid; the greater part of the free acid is driven off, the residue precipitated with potash and treated further as above.

For the analysis of nickel and cobalt ores, nickel glance, and for separating these metals from zinc, Professor R. Fresenius recommends the following two methods:—

Method I.—Applicable to nickel glance in particular.

An accurately weighed sample is fused with 8 times its weight of a mixture of equal parts of sulphur and sodium carbonate, the fused mass is treated with hot water, and the finely crystalline residue of metallic sulphides is filtered off and well washed, by which operation arsenic and antimony pass into solution.

After igniting the filter, the residue is treated with fuming nitric acid and evaporated to dryness. The small amount of lead sulphate remaining undissolved is not filtered off, but sulphuretted hydrogen gas is passed through the acid liquid till the latter is completely saturated with it. The filtrate from the copper and lead sulphides is evaporated to dryness, the ferrous oxide is oxidised with potassium chlorate, a little hydrochloric acid added, and the solution is then largely diluted, and sodium carbonate added till the reaction is nearly neutral, then acetic acid is poured in drop by drop, till a clear brown solution of iron and nickel acetates is formed. This done, the solution is heated to boiling, and when in that state the basic iron salt must at once be filtered off and washed. After this precipitate is redissolved, and again precipitated in the basic state as before, test a little of the precipitate to see whether it is free from nickel; if not, the above operation must be repeated till all the nickel is removed. The filtrates from the iron precipitate must be brought together and evaporated to a moderately small bulk. The solution is heated to boiling, and caustic potash is then added in slight excess. The hydrated nickel oxide is washed and ignited, and then reduced in a stream of hydrogen gas. The resulting metal is now brought on a small filter and treated with boiling water to remove any traces of caustic potash; after ignition of the filter it is again heated in a stream of hydrogen and weighed. The small amount of silica it contains is separated by dissolving the metal, evaporating the solution to dryness, and estimating the amount of silica, which is to be subtracted from the total quantity.

Method II.—Especially applicable to cobalt-nickel ores, and for the separation of zinc from those metals.

Instead of the fusion process, as described in Method I., the finely powdered ore is digested for some time with aqua regia and filtered.

The residue must be perfectly white, and if not so, must be fused with potassium bisulphate; the fused mass is then dissolved in hydrochloric acid and water, the solution filtered off, and the filtrate added to the principal one. The analysis is then continued exactly as in Method I.

Should the ore contain zinc the sample is treated as follows:—The nickel and cobalt sulphides are dissolved, the solution evaporated to a small bulk, and then ammonium chloride added in the proportion of 5 grammes—ammonium chloride to 0.2 gramme zinc; the mass is then evaporated to dryness on the water-bath till all the ammonium chloride is removed, and with it all the zinc. The remaining residue is treated with hydrochloric acid, a little nitric acid being also added; the solution is then evaporated to a very small bulk to remove the excess of acid, and then precipitated with caustic potash, and the analysis continued as in Method I.

When nickel and cobalt are to be examined *separately* evaporate the ammoniacal filtrate to dryness, remove the ammonia salts by gentle heating, dissolve the residue in hydrochloric acid, with addition of a little nitric acid, and when much nickel and little cobalt are present, estimate the latter as cobaltio-potassium nitrite; but if, on the contrary, there is much cobalt and little nickel, the solution of the chlorides of these metals is treated with potassium cyanide in excess, and after addition of pure caustic potash the nickel is precipitated warm as black hydrated nickel oxide.

In the first case the cobaltio-potassium nitrite, in the latter the nickel oxide, is dissolved in hydrochloric acid, and precipitated with caustic potash, and eventually estimated as metal.

Extraction of Nickel from its Ores.

The nickel ore usually met with is the arsenide, containing variable quantities of cobalt and iron, and frequently also copper and bismuth. It is finely powdered, mixed with 2 parts of solid caustic soda, and $1\frac{1}{2}$ part of sulphur, and fused in an earthen crucible, gradually increasing the heat to dull redness, at which temperature it is to be kept for some time. The mass is then digested in water, which dissolves the soluble sodium sulpho-arsenate, and leaves, when washed by decantation, crystallised nickel sulphide. Attack this with warm hydrochloric acid containing a little nitric acid.

The solution, heated to about 70°C ., is then submitted to a current of sulphuretted hydrogen, which must be continually passed until the liquid is cold. It is then to be covered over and left at rest for 24 hours; the arsenic, copper, and bismuth come down as sulphides. These are filtered off, and the filtrate is heated with potassium chlorate or sodium hypochlorite, to bring the iron to the state of sesquioxide, which is then precipitated by ebullition with excess of sodium acetate. The filtrate from the basic iron acetate is concentrated by

evaporation and mixed with a saturated solution of potassium nitrite,¹ which will precipitate all the cobalt.

The yellow precipitate washed with a saturated solution of potassium chloride may be treated as described below. The nickel is precipitated from the liquid either in the state of oxide by means of caustic potash, or after concentration, by a saturated and warm solution of potassium binoxalate. The precipitated oxalate, upon calcination, leaves pure nickel.

Purification of the Metallic Nickel of Commerce.

Dissolve the metal in hydrochloric acid, containing a little nitric acid. Pass sulphuretted hydrogen through the solution until the metallic impurities are thrown down, and then precipitate the nickel and cobalt by a warm saturated solution of potassium binoxalate. The precipitate, after being washed and calcined, leaves the nickel (containing a little cobalt) in the metallic state. Dissolve again in hydrochloric acid containing a little nitric acid, and separate by means of potassium nitrite.

Preparation of Metallic Cobalt from its Ores.

Metallic cobalt may be prepared from its ores (arsenide or sulphide) by a similar process to that adopted in the case of nickel (page 268). When the mineral contains more than 70 per cent. of arsenic, a preliminary fusion should be performed with sodium chloride to remove most of the arsenic. This may be continued by roasting or by fusion with a mixture of sodium carbonate and sulphur.

As nickel is almost invariably present in cobalt ores, this metal will require to be separated. Wöhler recommends for this purpose the potassium nitrite process (see above). The yellow cobalt precipitate is dissolved in as small a quantity of hydrochloric acid as possible, and sodium acetate is then added; the addition of a warm saturated solution of oxalic acid now precipitates the cobalt as oxalate. This oxalate, after being washed and dried, may be packed closely in a crucible of biscuit porcelain, protected by enclosure in a Hessian crucible. The covers being well luted on, the whole is heated in a wind furnace or a forge. If a sufficient temperature has been obtained, the cobalt will be in the form of a fused button.

Detection of Manganese in Presence of Nickel and Cobalt.

Manganese may be detected when in the presence of a very large excess of cobalt or nickel by means of Crum's test with Dr. Gibbs's

¹ Potassium nitrite is prepared by fusing, in an iron crucible, 1 part of nitre with 2 parts of granulated lead, stirring well with an iron spatula, and then heating to redness until the lead is completely oxidised. The fused mass, after cooling, is extracted with water, and the small amount of lead which is dissolved is precipitated by carefully adding a mixture of caustic ammonia and ammonium carbonate or sulphide.

modification (page 247). The solution of cobalt which is suspected to contain manganese is first to be freed as completely as possible from arsenic, copper, and iron. To a portion of this solution contained in a test-tube a solution of a pure nickel salt is to be gradually added, until the colour of the mixed fluid vanishes or becomes almost insensible. Nitric acid and lead peroxide are then to be added and the whole boiled for a few seconds, when the characteristic tint of a permanganate will appear, if but a trace of manganese be present. The same process is to be applied in testing solutions of nickel for small quantities of manganese, a pure solution of cobalt being added till the original green colour of the solution is destroyed. It rarely happens in the application of this method that a perfectly colourless solution can be obtained; usually the mixed solution has a faint brown tinge, like that of commercial sulphuric acid. This tint, however, has no sensible influence on the result.

In all cases where this test is employed the colour of the liquid must be observed immediately after boiling and subsidence of the excess of lead peroxide, as the tint fades when the solution is exposed to air and light.

Separation of Nickel and Cobalt from Manganese.

Dr. Wolcott Gibbs, to whom analytical chemistry is so greatly indebted, effects the separation of manganese from nickel and cobalt (and zinc also if present) in the following way:—To the neutral or nearly neutral solution of the chlorides, sodium acetate is to be added in excess, together with a few drops of free acetic acid. The solution is then to be boiled, and a rapid current of sulphuretted hydrogen passed through it while boiling, and continued for half an hour. Every trace of cobalt, nickel, or zinc is precipitated in the form of sulphide, while the whole of the manganese remains in solution. The precipitate is to be thrown on a ribbed filter and quickly washed with cold water saturated with sulphuretted hydrogen. It is easily washed, and though the cobalt sulphides and nickel precipitated in this manner are far more easily oxidised than when precipitated by boiling sodium sulphide from boiling solutions, they will be found to present no difficulty as regards oxidation upon the filter. Manganese may then be estimated in the filtrate by boiling with hydrochloric acid and precipitating in the usual manner with sodium carbonate. The mixed sulphides upon the filter—supposing, for the sake of generality, that all three are present—are to be dissolved in hydrochloric acid, and the metals converted into double cyanides by means of an excess of potassium cyanide, after which the zinc may be precipitated by means of sodium sulphide, as recommended by Wöhler.

When perfectly pure potassium cyanide is not at hand, the following process will be found particularly convenient:—Sodium acetate is to be added to the solution of the mixed chlorides, after which the

vapour of hydrocyanic acid, generated in a flask from sulphuric acid and potassium ferrocyanide, is to be passed directly into the solution. Zinc cyanide is immediately precipitated more or less completely as a perfectly white powder. A solution of sodium sulphide is then to be added as long as a precipitate is formed, after which the zinc sulphide is to be separated by filtration. Cobalt and nickel remain in solution as double cyanides. The same process may be used to separate manganese from cobalt and nickel, sodium sulphide throwing down under these circumstances a pure flesh-red precipitate. It is easy to see that zinc and manganese together may be separated from cobalt and nickel by the same process and at one operation. No manganese cyanide appears to be formed when hydrocyanic acid is passed into a solution containing a manganese salt, acetic acid, and sodium acetate.

The nickel and cobalt sulphides are thrown down from boiling solutions by a boiling solution of sodium sulphide in an insoluble form, so that, in fact, even strong hydrochloric acid scarcely exerts upon them an appreciable action. This process has been applied to the separation of cobalt and nickel from zinc and manganese by Mr. Perkins, and gives results which are very satisfactory, especially for qualitative purposes; the manganese and zinc sulphides precipitated under the same circumstances being readily soluble, even in dilute acid.

Separation of Nickel and Cobalt from Iron.

F. Field separates nickel and cobalt from iron peroxide by precipitating the latter with lead oxide. In the case of nickel and iron, the nitrates are evaporated nearly to dryness, and after the addition of water, lead oxide (litharge) is added, and the whole boiled for 10 minutes or a quarter of an hour. The iron is entirely precipitated, the nickel and lead nitrates remaining in solution. After filtration, which can be effected with great readiness, dilute sulphuric acid is added, and on standing for 16 hours the lead sulphate is filtered off, and the nickel precipitated and estimated in the usual manner. The filter containing the excess of litharge and peroxide is digested in dilute sulphuric acid, filtered, and washed. The filtrate is precipitated by potash.

It may here be remarked that nickel oxide can be more readily estimated by precipitation as peroxide by means of sodium hypochlorite than as oxide by caustic potash. Nickel peroxide, after boiling the solution in which it is suspended, separates as a rather dense precipitate, and can be easily washed, whilst the great difficulty of freeing the bulky gelatinous protoxide from potash is well known. The alkali, indeed, adheres with remarkable pertinacity to this substance, and if not added with considerable caution, and other circumstances attended to, very protracted washing is necessary. In employing sodium hypochlorite, it is requisite to have an open vessel, a beaker for instance, as the peroxide is liable to form flakes upon the sides of the glass, which

are difficult to remove from a narrow-necked flask. The peroxide is heated to whiteness and the nickel weighed as protoxide.

Cobalt can be separated from iron in precisely the same manner as nickel. Many analyses have shown that no trace of cobalt is precipitated from its solution on boiling with lead oxide, and even when the iron is in considerable excess—50 to 1 for example—the separation is complete. The solution of cobalt freed in this manner from iron contains no trace of that metal, gives no shade of blue with potassium ferrocyanide, nor can iron be recognised by any known test.

Wöhler separates nickel and cobalt from iron peroxide by adding a large quantity of ammonium chloride and then excess of ammonia. The iron sesquioxide is precipitated, whilst the nickel and cobalt remain in solution. Slight traces of the latter metals are, however, carried down by the iron.

Iron sesquioxide may be perfectly separated from cobalt and nickel by boiling the neutral or nearly neutral solutions with sodium acetate, provided that the following precautions are observed:—The solutions from which the iron is to be precipitated must be dilute; half a litre of the solution should not contain more than 1 grain of the sesquioxide. The quantity of sodium acetate should be sufficient to convert by double decomposition all the bases present into neutral acetates. The acetate should be added to the metallic solution when cold, and the whole should then be heated together and boiled for a short time. It is not necessary to filter upon a water-bath funnel, but the beaker containing the solution should be kept nearly at the boiling-point during filtration, and a ribbed filter should be employed. It is especially necessary, where nickel is present, to add a few drops of free acetic acid to the solution, to prevent the formation of basic acetates of the protoxides. Finally, it is best, whenever possible, to have all the bases present in the form of chlorides. The iron upon the filter in the form of basic acetate must, whenever an absolutely complete separation is necessary, be redissolved in hydrochloric acid, and again be precipitated by boiling with the acetate after rendering the solutions nearly neutral by means of sodium carbonate. In this manner only it is possible to separate the last traces of the stronger bases. Finally, the basic iron salt, after washing, must be redissolved in hydrochloric acid, and precipitated by boiling with ammonia in the usual manner, to free it completely from alkali.

Mr. T. Moore recommends that if the solution contains much free acid, this should be got rid of by evaporation and dissolving the residue in water. To the solution so obtained a quantity of ammonium sulphate should be added, sufficient to form a double sulphate with the nickel and cobalt present. Dilute to about 150 c.c., and then add rather a large excess of oxalic acid, and stir well. If a precipitate forms, more ammonium sulphate must be added until a clear solution is obtained. Ammonia is now added in considerable excess; stir, heat

gently for a few minutes, and filter; wash well with water containing ammonia; or dilute to 500 c.c., and after allowing the precipitate to settle, withdraw a given portion of the clear upper stratum of liquid, which, after a further addition of ammonium sulphate (to lessen the resistance of the solution to the electric current), is ready for electrolysis or any other method of estimating the nickel or cobalt the chemist may desire.

Separation of Nickel or Cobalt from Zinc.

M. Brunner gives the following solution of this problem:—The solution of the two metals (zinc and nickel, or zinc and cobalt) in hydrochloric or nitric acid, is diluted with a large quantity of water, and almost completely neutralised by sodium carbonate. To effect this, a slight excess of the latter is added, and the precipitate which ensues is redissolved in a few drops of acid, so as to introduce a very slight excess of the latter. A current of sulphuretted hydrogen is then made to pass through the liquid, and to complete the precipitation of the zinc, a few drops of a diluted solution of sodium acetate are added to the liquid. Care must be taken not to introduce an excess of acetate, and not to heat the liquid. A fresh current of sulphuretted hydrogen is now allowed to pass, until the precipitate does not appear to increase. The vessel is then left to itself for 10 or 12 hours at the ordinary temperature, after which the precipitate is collected on a filter and washed. To make sure that all the zinc has been thrown down, a drop of sodium acetate may be added to a little of the filtered liquid, which should remain clear when a little sulphuretted hydrogen is introduced. The nickel or cobalt is thrown down from the filtrate by potash. If the original solution contain iron, it is essential to separate it first of all by barium carbonate.

A very good plan for separating nickel from zinc is given by Wöhler as an illustration of the method of analysing German silver (an alloy of nickel, zinc, and copper):—The copper having been separated from the other metals (see Copper), the liquid, after being filtered and reduced, by evaporation, to a small bulk, is treated by excess of caustic potash, and then by hydrocyanic acid, until the precipitate which is at first formed is completely redissolved with a yellow colour. In this liquid, which contains double cyanides, the zinc is precipitated in the state of sulphide, by means of potassium protosulphide (not ammonium sulphide). After some hours' digestion, and when the precipitate is completely deposited, it is filtered off, and, after boiling the liquid with aqua regia, the nickel is precipitated as oxide by caustic potash. This oxide must be calcined after it is dried.

Separation of Nickel or Cobalt from Uranium.

Dr. Gibbs's method already given for the separation of manganese from cobalt, zinc, and nickel, by precipitating the sulphide of the three last-named metals by means of sulphuretted hydrogen from a boiling solution of the acetates (page 270), may be also used for the separation of uranium from the same metals. The process is in all respects the same, and requires, therefore, no further description. It will be found much simpler and more convenient than that described by Rose, by means of barium carbonate.

Separation of Nickel, or Cobalt, from Manganese, Iron, Zinc, and Uranium.

Clemens Zimmermann, after pointing out that the usual procedures are either very tedious or questionable as to accuracy, gives his method for separating zinc from other metals of the group by means of ammonium sulphocyanide. To the liquid in question, which, in addition to the zinc salt, may contain any number of the other metals of the fourth group, iron and uranium, if present, being in the state of ferric and uranic salts, he adds, if its reaction is acid, sodium carbonate till a slight turbidity appears, neutrality being the main condition for success. An excess of a solution of ammonium sulphocyanide, not too dilute, is then added, the sides of the vessel are rinsed with water at 60° to 70°, preferably by means of an Erlenmeyer flask, and a very moderate stream of sulphuretted hydrogen is introduced repeatedly, but not for very long, till the odour of this gas does not disappear after the liquid has stood for some time. During the introduction of the gas the appearance of a milky-white precipitate is first perceived, and after a considerable time zinc sulphide is separated in flocks which continually become denser. The beaker is now exposed to a gentle heat till the precipitate has settled and the liquid has become clear, which may require 6 hours. It is then filtered, the white zinc sulphide is washed with water containing sulphuretted hydrogen and ammonium sulphocyanide, and dried. This precipitate contains all the zinc, free from the other heavy metals of the group. When dry it may be ignited in a current of hydrogen according to Rose's process, or it may be dissolved in hydrochloric acid, evaporated to dryness in a weighed platinum capsule on the water-bath, mixed with an excess of elutriated mercuric oxide, pure, and free from alkali, evaporated to dryness, and ignited. Zinc oxide remains, perfectly pure and without loss, and is weighed when cold.

In the filtrate from the zinc sulphide the sulphocyanides are first destroyed by means of nitric acid, which at the same time peroxidises any ferrous or uranous salts present. This operation is best effected in a roomy, long-necked flask, which is heated on the water-bath,

and nitric acid added by degrees in small portions until the liquid no longer becomes red, followed by decolouration. Any yellow cyanogen persulphide formed is filtered off. If the acid is added too rapidly the liquid may be projected from the flask.

In order to separate the iron present from nickel and cobalt, the solution, which may contain ferric salts along with nickel or cobalt salts or both, is mixed with an excess of ammonium sulphocyanide, when the blood-red colour of iron sulphocyanide appears; a dilute solution of sodium carbonate is then added, drop by drop, till the red colour just disappears. All the iron is thus precipitated as ferric hydroxide, none of it remaining in solution, and no cobalt or nickel being thrown down. The precipitate is allowed to settle, filtered, washed with boiling water, to which a little ammonium sulphocyanide has been added, dried, ignited, and weighed. The filtrate is treated as has been directed for the filtrate from zinc sulphide. The author separates cobalt and nickel by Liebig's method with ferric oxide.

For the separation of iron and uranium the liquid, in which the metals must have been peroxidised, is brought to a boil, mixed with an excess of ammonium sulphocyanide, and aqueous sodium carbonate is added, exactly as above directed for the separation of iron from cobalt and nickel. The same process is further followed for the removal of the iron, which is found free from the slightest trace of uranic compounds.

The filtrate which contains uranic oxide in solution is first treated with nitric acid to destroy the sulphocyanogen, then neutralised with ammonia, and mixed with ammonium sulphide; the precipitate of uranium oxysulphide is boiled, by which it is resolved into sulphur and uranous oxide, filtered, dried, and ignited. Lastly, the uranium is either weighed as uranoso-uranic oxide, or converted into uranous oxide by very strong ignition in a current of hydrogen gas, which is maintained until the product is cold. The precipitation of uranic oxide by ammonia is greatly promoted by the addition of ammonium chloride, without which it does not take place in dilute solutions.

The Behaviour of Sulphuretted Hydrogen with the Salts of the Heavy Metals.

H. Delffs calls attention to the different precipitability of metallic salts in presence of any strong mineral acid on the one hand, and of acetic acid on the other. Just as the limit between precipitable and non-precipitable salts is altered by the use of acetic acid instead of hydrochloric acid, it is further modified if formiates are treated with sulphuretted hydrogen. In that case the zinc salt is precipitated, but the cobalt, nickel, iron, and manganese compounds are not affected. Manganese cannot be thrown down by sulphuretted hydrogen

from propionic, butyric, and valerianic solutions. In precipitations by sulphuretted hydrogen several metals are never simultaneously converted into the corresponding sulphides, but the precipitation ensues in such a manner that one metal is first completely separated before the removal of another begins. Upon this fact is founded a very convenient method for obtaining cobalt and nickel in a state of purity. As sulphuretted hydrogen first completely precipitates cobalt acetate, and then acts upon nickel acetate, a solution of the two nitrates is mixed with sodium acetate in quantity insufficient for complete double decomposition, and sulphuretted hydrogen is introduced, so that according to the respective proportions of the two metals either nickel free from cobalt is obtained in solution, or cobalt free from nickel as a precipitate. The more electropositive a metal is the later it is precipitated from a mixture of its salts with those of other metals.

CHAPTER VII.

SILVER, MERCURY, COPPER.

SILVER.

Preparation of Pure Silver.

THE subject of the preparation of pure metallic silver has been studied in so exhaustive a manner by Professor Stas in his researches on the relations existing between atomic weights, that there is little left for any other investigator to do in connection with this subject. In the following pages are given an abstract of the processes which he found more successful. All the methods hitherto recommended for the preparation of pure silver which are capable of being executed on a large scale furnish an impure metal, unless important modifications are introduced.

Preparation of Silver from Silver Chloride.—All processes which depend upon the reduction of silver chloride yield a metal containing copper and iron, unless, indeed, it has been redissolved three or four times successively in nitric acid, the solution, after diluting with 20 or 80 times its weight of water, being each time poured into aqueous hydrochloric acid, and the silver chloride violently agitated in the liquid, as in the process of assaying. Experience has shown that silver chloride, free from copper and iron, can be obtained directly by pouring a cold solution of silver nitrate diluted with 90 times its weight of water, into a slight excess of hydrochloric acid, washing the precipitate with cold distilled water, and then digesting the chloride, dried at the ordinary temperature, and finely powdered, in aqua regia. When well washed after this treatment, the chloride does not retain the slightest trace of either copper or iron; whilst, so long as the silver chloride is in a curdy form, it retains in its pores, like coagulated albumen, some of the bodies which were dissolved in the liquid from which it was precipitated. Silver chloride, however, when dried at the ordinary temperature and finely powdered, very easily yields to aqua regia foreign metals which contaminate it. But whatever may be the purity of silver chloride, it produces a metal which always contains silicium and iron when it is reduced by Gay-Lussac's method; that is to say, by ignition with a mixture of chalk and charcoal.

The presence of these foreign matters is easily ascertained by

dissolving 100 grammes of silver in pure nitric acid in a platinum dish, and evaporating and fusing the nitrate. On dissolving the salt in cold water there is always a residue of silicic acid and iron sesquioxide. M. Stas says that he has found as much as $\frac{1\frac{1}{2}}{100000}$ of silicium in silver reduced from the chloride by Gay-Lussac's process.

It is probable that the presence of so large a quantity of silicium in the metal so prepared is due to the action which silver has upon silicic acid. At the temperature necessary for fusion silver may reduce the silicic acid with formation of silver silicate and silicide. Furthermore, the presence of carbon may favour the reduction of silicic acid and the formation of silver silicide. One thing is certain, that the vapour of silver attacks silicic acid and the silicates. White porcelain becomes coloured yellow or yellowish-brown, and increases very sensibly in weight, when there is directed upon it the vapour of silver driven off before the oxyhydrogen blowpipe.

Silver chloride, purified by the above process, mixed with its own weight of pure dry sodium carbonate, containing a tenth part of pure potassium nitrate, when heated in a white unglazed porcelain crucible, with the precautions recommended by Berzelius for avoiding intumescence, yields an ingot of silver. This ingot, fused again with a tenth of its weight of pure nitre and borax, and then run into an ingot-mould lined with pipeclay, gives a bar of silver which retains scarcely any appreciable traces of foreign matters. This process requires great care, for when the mixture of chloride and carbonate is heated, if the temperature is raised too much at first, the mixture fuses, bubbles up, and is in danger of running over. To effect with safety the reduction of silver chloride in a white unglazed porcelain crucible, the latter should be placed inside a clay crucible. The most convenient plan for performing this operation is the following:—Fill up the space between the two crucibles with calcined pipeclay, powdered and mixed with 5 per cent. of fused and powdered borax. Under the influence of the heat the borax fuses and solders the whole together. When the silver chloride is reduced, the whole can be handled and the melted silver poured out as if it were one crucible. The great bulk which has to be heated before reaching the porcelain crucible prevents it cracking, and avoids loss of silver.

Preparation of Silver by Liebig's Process.—This process consists in reducing in the cold, by means of pure milk sugar, a pure concentrated ammoniacal solution of silver nitrate, to which pure potash has been added, until fulminating silver begins to be precipitated. After a short time a violet precipitate is formed, which is transformed into a mirror of silver, if the solution does not contain more than 10 per cent. of nitrate. If, on the contrary, it contains much more metal, the silver remains as a violet precipitate. This precipitate, after being washed with water, is digested with aqueous ammonia, which removes the copper, if the silver contained any.

When dried, it preserves its violet colour, and constitutes a peculiar modification of silver. Heated to 800° or 850° C., the metal becomes incandescent, and then assumes its proper colour, being of a dead white. To reduce it to bars fuse it with a certain quantity of pure nitre and borax, and run it into an ingot-mould lined with pipeclay. This always gives the metal of a uniform purity. It must be borne in mind that it is not only necessary for the metal obtained by any process always to possess the same properties; it is also necessary for it to be absolutely identical with pure silver prepared by other methods. For it may happen—and this is the case in the reduction of pure silver chloride by Gay-Lussac's process—that the operation of reduction communicates to the metal as much impurity as has been separated by solution and precipitation.

Preparation of Silver by Electrolysis.—Another plan consists in procuring the metal by the electrolysis of pure potassium or ammonium argento-cyanide. This method is, however, long and very costly. The deposit is made upon a surface of porcelain previously covered with a mirror of silver, by Liebig's method. For a positive electrode coke is used, obtained by heating the vapour of naphtha to redness. To obtain a silver nitrate fit to prepare the cyanide, dissolve in nitric acid silver assaying 999. Evaporate the solution to dryness and fuse the salt. After cooling, powder, and digest it in cold water, taking care not to dissolve it all, for otherwise copper oxide would come into solution. The solution of silver is allowed to stand for 8 or 4 days, filtered through double filter-paper, then digested with an excess of silver oxide, and allowed to remain at rest for a sufficient time. This solution is diluted with water until it only contains a thirtieth part of its weight of nitrate, and poured into pure aqueous hydrocyanic acid until cyanide is no longer precipitated. The cyanide is shaken in the liquid to finely divide it, and then washed with water acidulated with nitric acid, and finally with pure water. The cyanide is diffused in an amount of aqueous hydrocyanic acid equal to that used in its precipitation, and then pure ammonia or potash is added to the mixture until the cyanide is all dissolved. When undergoing electrolysis the positive pole of carbon is surrounded with silver cyanide, contained in a linen bag purified by means of hydrochloric acid. Silver is thus returned to the liquid as fast as it is removed by electrolysis. M. Stas says that he has been unable to find any foreign body in this silver after it has been fused in an unglazed porcelain crucible with a mixture of purified nitre and borax.

Preparation of Silver by Precipitation with Phosphorus.—An excellent, although very slow, method for preparing perfectly pure silver is by acting on a 1 per cent. solution of silver nitrate with finely divided phosphorus. This action is very slow, but the metal, after having remained for a long time in an excess of solution of silver,

and then being digested in ammoniacal water, yields, after fusion with purified nitre and borax, silver absolutely pure.

Preparation of Silver by Reduction of the Chloride in the Wet Way.—Dissolve at the boiling-point a silver coin in very dilute nitric acid. The silver nitrate produced, after having been evaporated to dryness and fused, is kept at its point of fusion as long as any oxygen compounds of nitrogen are given off. The nitrate mixed with nitrite is dissolved, when cool, in the smallest possible quantity of cold water, and the solution, after resting 48 hours, is filtered through a double filter to separate all the matter that might have remained in suspension. The limpid solution, diluted with 80 times its volume of distilled water, is precipitated by an excess of pure hydrochloric acid. The silver chloride formed is, when deposited, washed by decantation, first with water acidulated with hydrochloric acid, and then with pure water.

This washing is performed by shaking the chloride violently each time in large stoppered bottles, with the necessary quantity of liquid.

It is then spread upon a cloth that has been washed with hydrochloric acid, strongly compressed and left to dry spontaneously. When perfectly dry it is finely powdered and digested for several days in aqua regia. It is then again washed in distilled water.

As the reduction by heat of silver chloride with sodium carbonate is a most delicate operation, when performed in large quantities, this reduction is effected under the influence of a solution of caustic potash and sugar of milk, as first proposed by Levol.

To procure potash and sugar of milk free from heavy metals, add to a concentrated solution of potassium hydrate, previously boiled, a slight excess of a solution of potassium sulphhydrate to precipitate traces of dissolved metals.

After the deposit of the metallic sulphides, decant the alkaline solution and put it in contact with freshly precipitated silver oxide, to deprive it of sulphur; after a sufficient digestion and rest, separate the excess of silver oxide and the silver sulphide that has been produced. By the same means the heavy metals contained in an aqueous solution of sugar of milk are eliminated.

The silver chloride contained in a large porcelain jar is digested at a temperature of from 70° to 80° C. with a mixture of solutions of potassium hydrate and sugar of milk, until all the chlorine is separated from the silver. The metallic silver, which is grey, is washed with water until the excess of alkali has disappeared, then digested with pure dilute sulphuric acid, and lastly washed with ammoniacal water. After being dried, 5 per cent. of its weight of borax is added, containing 10 per cent. of sodium nitrate, and then, with necessary precautions, it is fused in a Paris crucible.

The fused metal may then be poured into a mould coated with a paste of mixed calcined and uncalcined kaolin. The bars of silver, first

cleaned with sharp sand, are then heated to redness with caustic potash prepared from tartar; the adhering kaolin having been dissolved, the bars are washed in pure water.

Preparation of Pure Silver by Reduction of its Ammoniacal Solutions.—This method furnishes pure silver more easily and promptly than any other known way; and it has the special advantage of giving it in a state of great purity. It is based upon the complete reduction which ammoniacal solutions of silver compounds undergo when added to ammoniacal cuprous sulphite, or to a mixture of ammonium sulphite and any ammoniacal copper salt. At the ordinary temperature this reduction takes place slowly, with deposition of black, blue, or grey silver, according to the dilution of the liquids. Above a temperature of 60° C. the reduction is almost instantaneous, and the silver is precipitated in a state of division corresponding to the dilution of the liquid; its colour varying from grey to pure white.

A silver coin is dissolved in dilute and boiling nitric acid; the solution of silver and copper nitrates is evaporated to dryness, and the saline mass fused. This fusion is necessary to destroy the platinum nitrate, which is often formed in dissolving silver coins.¹ After cooling, the nitrates are taken up by an excess of ammoniacal water. The ammoniacal solution is left to rest for 48 hours. The limpid liquid is filtered through double filter-paper, and then diluted with distilled water until it contains no more than 2 per cent. of its weight of silver.

Neutral ammonium sulphite is obtained by mixing ammonia with sulphurous acid. To ascertain the quantity of sulphite required for the complete precipitation of the silver from the ammoniacal solution of silver and copper nitrate, heat to the boiling-point a definite volume of solution of ammonium sulphite, and ascertain the volume of the solution of silver and copper which is decolourised by this salt. Experiment has proved that, as soon as the ammonium sulphite, sufficiently heated, is not coloured blue by the cupric oxide dissolved in the ammonia, there remains no trace of silver dissolved in the liquid, because in this case all the copper exists in the cuprous state, the presence of which is incompatible with that of any compound of silver dissolved in ammonia.

The quantity of ammonium sulphite necessary for the precipitation of the liquid having been ascertained, add it to the argentiferous solution, and after being well mixed leave it to itself for 48 hours in a closed glass flask, to prevent the contact of the air. At the end of this time about a third of the silver will be reduced, at the ordinary temperature, and is precipitated in the form of a shower of crystallised silver, of a greyish-white colour and very brilliant.

The decanted blue liquid, in quantities of 10 litres at a time, is

¹ Silver coins frequently contain iron, nickel, and traces of cobalt, platinum, and gold.

then put into a water-bath at a temperature of from 60° to 70° C. The time required to cause the elevation of temperature is quite sufficient for the complete reduction of the remainder of the silver in solution, and for the reduction of the cupric sulphite to the state of cuprous sulphite, especially if care is taken to have a sufficient excess of solution of ammonium sulphite. The liquid in which the reaction takes place becomes quite colourless if the copper contains neither nickel nor cobalt. If it contains nickel, it takes a slight green tint; it takes, on the other hand, a reddish tinge if cobalt is present.

The silver being separated out, decant the liquid when cold, and wash separately the silver precipitated from the cold and the warm solutions. This washing is performed by decantation with ammoniacal water; it is continued as long as the washing waters are perceptibly coloured blue by exposure to air, or are precipitated by barium chloride. The silver is afterwards left for several days in concentrated ammonia, and then washed in pure water.

If the solution from which the silver is precipitated has been diluted until it contains no more than 2 per cent. of silver, the ammonia left in contact with this metal is not coloured even after several days' digestion. There is no longer any copper for the ammonia to dissolve; it dissolves silver instead, for this metal is feebly attacked by the alkali under the influence of air, as is easily proved by evaporating liquid ammonia which has remained for several days in contact with turnings of pure silver. The liquid always leaves a black shining mirror of silver nitride by its spontaneous evaporation.

By fulfilling all the conditions above described, and especially by carrying the dilution of the ammoniacal solution of the silver and copper nitrates to 2 per cent. of silver, we obtain silver of great purity. When the precipitated silver is required in bars, fuse it with 5 per cent. of its weight of calcined borax containing 10 per cent. of sodium nitrate, as mentioned in the case of the silver reduced from the chloride by potash and sugar of milk. Larger quantities may also be fused with the aerhydrogen blowpipe in a crucible of pure porcelain, or in an oxyhydrogen gas furnace in crucibles of marble-lime.

Purification of Silver by Distillation.

Pure silver may be fused in air at a temperature sufficiently high to volatilise it, without becoming at all stained or discoloured, and without giving off coloured vapour. This fact has been taken as a basis by Professor Stas, in order to ascertain the purity of the silver prepared by either of the processes already given. He describes his experiment as follows:—About 400 grammes of silver reduced from its chloride, placed in a crucible of lime from white marble, itself enclosed in a refractory crucible, were submitted to the hissing flame produced by the combustion of ordinary coal gas with pure oxygen. The silver fused without becoming in the least discoloured. It was then heated

until it boiled violently. The silver first gave to the flame the sodium character ; but in a short time the yellow colour disappeared, and, so long as the silver did not boil, no discolouration appeared, although the metal gave off vapour in considerable quantity. After the silver boiled, a pale blue vapour was produced, which occasionally bordered upon purple. Some chemists assign a green colour to the vapour of silver. The green colour observed arose indisputably from the copper contained in the silver submitted to the experiment. The purple colour is attributed to the existence of strontium or lithium in the marble used for the preparation of the quick-lime crucible.

This vapour stained the lime a deep yellow, which colour, however, disappeared on the application of heat. When, by this process of refining, the silver had lost all volatile matter, and when the fixed but oxidisable materials that it might contain must have united with the lime, it was poured from a good height, and in a thin stream, into distilled water, where it took the form of pure white, almost spherical globules. The crucible presented no trace whatever of a metallic oxide or silicate.

The same treatment was applied to the pulverulent silver prepared by the cuprous ammoniacal sulphite, and identical phenomena presented themselves, excepting always the intense yellow colour of the flame, which was produced when the silver reduced from the chloride was heated to near its boiling-point.

Before submitting the silver under experiment to the action of the oxyhydrogen gas-flame care must first be taken to expose the lime-crucible to the heat of the oxyhydrogen blowpipe, so as to eliminate as much as possible from the lime the volatile substances that give a particular colour to the flame ; all marbles contain notably sodium, and many contain strontium and lithium.

Having been struck by the facility with which silver may be boiled violently, and distilled in the flame of oxyhydrogen gas, Professor Stas was led to experiment on the distillation of silver both for the object of obtaining it absolutely pure, and also to ascertain if silver refined by the methods already described still retains any traces of fixed bodies capable of uniting with lime.

For this purpose, in a block of lime prepared from white marble, of from 25 to 30 centimetres in length, by 10 centimetres width and height, there was made a circular cavity 3 centimetres in diameter and 2 centimetres in depth, in communication with an inclined plane also 3 centimetres in width, by at most half a centimetre in depth, and serving to condense the vapour of silver. This inclined plane was terminated by a reservoir acting as a receiver for the liquid metal. About 50 grammes of refined silver were placed in the cavity, first heated to whiteness by the application of a jet of coal-gas burning in a suitable excess of compressed air, and the block was covered with a plate of lime from white marble, 5 centimetres in thickness, pierced

with two inclined circular openings, one corresponding to the circular cavity, the other to the little reservoir at the end of the inclined plane. Through one of the openings of the plate was passed a large oxyhydrogen blowpipe, furnished with very thick ends of platinum to avoid their fusion and the transportation of the metal. When the interior of the cavity had been heated to the boiling-point of silver, not more than 10 or 15 minutes were required to distil the whole of the silver. The 50 grammes were volatilised without leaving in the cavity of lime, which was used as the retort for distillation, the slightest appreciable residue to the eye assisted by a glass. The distillation of silver is such a simple operation to manage that nothing could be easier than to procure a kilogramme of distilled silver, if the apparatus was proportioned to the mass. In the operations above described, *at least* half the silver used was, however, lost. It was, in fact, carried away in the state of pale blue vapour by the current of oxyhydrogen gas, although this was very moderate, and without too great an excess of oxygen; it was diffused through the surrounding atmosphere, the transparency of which it affected, while imparting to it a very sensible metallic taste. The apparatus was also very imperfect; vapour of silver escaped in quantities by the opening intended to carry off the products of combustion, and all round between the block and the thick plate serving as a cover to it. Their surfaces, indeed, were not sufficiently well smoothed to fit very exactly. Wherever the vapour of silver passed it left a light or dark yellow stain, like that left by the vapour of litharge. The condensation of the vapour of silver takes place the more readily the less excess of oxygen the oxyhydrogen gas contains.

All the different samples of silver prepared by any of the above described methods were subsequently fused, and cast in an ingot-mould lined with white pipeclay. To detach the pipeclay, the surfaces of the bars were rubbed with sharp white sand. They were then heated to dull redness and covered over with caustic potash, which was kept in a fused state for at least a quarter of an hour. The adherent pipeclay being in this manner attacked, the bars were suddenly plunged into water. The silicate formed on the surface being thus detached, the bars, after a second scrubbing with sharp sand, were fit for use. These bars, before being employed, were treated with boiling hydrochloric acid, washed first in cold aqueous ammonia, then in pure water, and finally heated to redness on plates of pure silver. It having been necessary for the silver to be in the form of small lumps, from 2 to 25 grammes in weight, in the form of sheet, and in a certain state of division to make up weights previously calculated; the small lumps were obtained by cutting the ingots with a chisel on an anvil of polished cast-steel. The turnings and filings obtained from the ingots by means of a lathe and file furnished the finely-divided silver. To separate the iron adhering to the silver when cut with the chisel,

lathe, or file, these different forms of the metal were digested in a close vessel for 24 hours, and at a temperature of 60° to 80° C., first with strong hydrochloric acid, and then with pure ammonia. The silver was finally washed with absolutely pure water, heated to redness on a plate of pure silver, and immediately put into bottles with well-fitting stoppers. Having found that silver, after having been rolled, contained iron, which was absent before rolling, the precaution was taken to have all the silver which was required in the form of sheet rolled between two plates of pure silver. It is only at the expense of the surfaces of the two plates which touch the cylinders of the mill that the surface of the inner plate could be protected from contamination with all foreign metal. The laminated silver was heated to redness in the air, and enclosed whilst very warm in a well-stoppered bottle.

Ascertaining the Purity of Silver.—Professor Stas gives a very simple plan for ascertaining the purity of silver. The pure metal remains melted in the air at a sufficiently high temperature to volatilise it without being covered by any scum or colouration, and without giving a coloured vapour. Silver containing no more than the $\frac{1}{100000}$ part of iron, copper, or silicium becomes covered with a very strong and mobile scum when it is fused before a blowpipe, fed with a mixture of illuminating gas or hydrogen and an excess of air. Silver containing scarcely appreciable traces of copper when volatilising in an oxidising flame always gives a coloured flame. This assay may be performed on charcoal or white-burned pipeclay, or on porcelain, by means of a gas blowpipe or a simple eolipyle. The scoria derived from the impurities in the metal always forms upon the surface of the flattened spheroid caused by the fusion. After cooling, the foreign matter is found adhering to the silver near the point of contact of the metal with the support.

Estimation of Silver in the Metallic State.

According to Dr. A. Classen, silver is wholly precipitated by cadmium. When dealing with a nitric solution of silver, evaporate to dryness in the presence of sulphuric acid, dissolve the silver sulphate in boiling water, plunge into it a plate of cadmium, and the reduction of the silver takes place at once. The silver is deposited in a compact mass, easily washed with water; as it may contain a little cadmium, boil it in the acid liquid until no hydrogen escapes; wash it until the water contains no sulphuric acid; then dry and calcine; the silver, at first a black grey, takes the metallic lustre; it may then be weighed—the results are very exact.

The reduction of silver compounds by means of cadmium goes on very quickly, and as cadmium is but slightly soluble in dilute acids, the same piece of metal will serve for several operations, without even losing the metallic lustre of the surface. Freshly precipitated silver chloride may be reduced in the same way.

Volumetric Estimation of Silver.

It would be out of place here to describe the well-known Gay-Lussac process for the assay of silver by the wet way. It is necessary, however, to draw attention to some recent improvements introduced into this process by Professor Stas, by which the errors incidental to the old process are entirely obviated. The operation is conducted in the following manner:—The silver, after having been heated to redness in a crucible of the same metal and properly cooled in the air, is weighed and introduced into a white glass flask, with the stopper well ground in with emery, and having very thick sides to enable it to withstand an internal pressure of at least 10 atmospheres. Then pour upon the metal 10 times its weight of pure nitric acid at 25° Baumé. Put in the stopper and fix it solidly in its place by the aid of strong cord. Then surround the flask with wire gauze, and place it in a bath where its temperature is raised to 45° or 50° C. At the end of 24 or 36 hours all the silver will have dissolved without any trace of gas developing itself, and consequently without anything escaping from the flask. Indeed, the nitrogen binoxide, as fast as it is produced, reduces the nitric acid to the state of nitrous or hyponitric acid, which at this temperature remains perfectly dissolved in the large excess of nitric acid employed. If the temperature of the bath does not exceed 50°, there is nothing to fear. Upwards of 100 solutions of silver in a closed flask have been made, employing from 3 to 50 grammes of silver at a time, without any accident taking place. Twice only, the temperature of the bath rising much too high, two flasks which were immersed in it yielded to the internal pressure and produced a rather violent explosion. The plan of dissolving the silver in a close vessel has been adopted because the method of solution in open vessels, such as is adopted in the assay-rooms of the Mint, causes a slight loss of silver. Moreover, the constant presence of silver in the washing-waters of the gas, arising from the solution of the metal in the ordinary way, sufficiently point out the necessity of effecting this solution either in a close vessel or in apparatus in which the escaping gases may be washed. It ought to be added, however, that the loss experienced upon a gramme of silver never affects the accuracy of the assay of silver in the Mint, owing to the much more considerable and unavoidable errors of experiment.

The remainder of the description is given in Professor Stas's own words:—‘The solution of the metal having been effected, and the flask well cooled, I introduce such an amount of pure water that, with the acid already added, the total weight of the liquid becomes at the minimum 35 times, and at the maximum 50 times, the weight of the silver employed. I now carry the flask into a dark room lighted with gas. After having conveniently inclined it, I introduce it into a tube, sealed up at one end, fixed to a rod of platinum, and containing the chloride

weighed with the greatest accuracy which my balances will admit of. I then drop the chloride into the solution of silver, and wash the tube out several times with water, so as not to lose the traces of chloride which may remain adhering to it. After having tightly closed the flask, and enveloped it in caoutchouc, I shake it until the liquid, at first turbid, becomes perfectly clear. I then proceed to the assay of the silver remaining unprecipitated. For this purpose I have prepared with the greatest care the decimal solutions of salt and silver, such as are employed in the laboratories of the Mint.

‘On the other hand, I have myself manufactured pipettes, tubes which when empty in a vertical position, would furnish me 10, 5, 4, 3, 2, 1, or $\frac{1}{2}$ a cubic centimetre of decimal solution. I also constructed burettes, which, when placed in a vertical position, would deliver drops exactly equal to the twentieth of a cubic centimetre. The burette itself and the tubes of $\frac{1}{2}$, 1, and 2 centimetres, are subdivided into twentieths of a cubic centimetre. The small burette consists of a graduated tube of 4 or 5 millimetres internal diameter, drawn out to a point so as to expose an opening of about 1 millimetre in diameter, and melted to a larger open tube, the aperture of which is covered with a piece of vulcanised caoutchouc folded over the side of the tube, and more or less strongly bound to it, according as it is wished to deliver the drops more or less rapidly; my burettes would only give 5 or 6 per minute.

‘It is absolutely necessary to hold the burettes in a vertical position, for the same instrument which furnishes with the greatest accuracy 20 drops per cubic centimetre only delivers 17 or 18 when it is inclined 45° ; in a position of 10° or 15° no more than 16 or 17 drops are required to make a centimetre.

‘To perform the assay, I had besides the following arrangement:—In a long narrow box, the anterior portion of which was furnished with yellow glass, and the posterior portion lighted by a gas lamp, I arrange a perfectly spherical glass globe containing a saturated solution of the double potassium and sodium chromate, so as to concentrate the rays and obtain a cone of yellow light. I then place the flask containing the assay in such a position that the surface of the liquid may be traversed by the beam of yellow light. To make an observation, I place myself so as to make an angle of 60° with the luminous ray traversing the flask. When this artifice is employed, a liquid containing 2 milligrammes of silver per litre produces a yellow opaque and dull precipitate of silver chloride, when half a centimetre of decimal solution is allowed to fall carefully upon its surface; when the quantity of silver is reduced to 1 milligramme, the precipitate of chloride is yellow, opaque, and brilliant; when the liquid is diminished in strength, so that it contains no more than the twentieth of a milligramme of silver per litre, there is still produced an appreciable cloud upon the addition of a corresponding quantity of decimal solution. It is only necessary to wait sufficiently long, without touching the flask,

to be certain of it. Nevertheless, in these assays I have only worked to tenths of a milligramme.

'In all my experiments I have continued adding decimal salt solution as long as I have seen a cloud produced on the surface of the liquid after standing 15 minutes. When I have arrived at the extreme limit, and have just passed it, I add 5 centimetres of decimal solution of silver. After well shaking, I neutralise three-quarters of the excess of silver, so as to obtain immediately upon agitation a clear liquid approaching very nearly the extreme limit. When there was a difference between the results of two assays, a difference that has never exceeded $\frac{1}{10}$ or $\frac{3}{10}$ of a milligramme, I always took the minimum result.

'Those who have made many assays by the wet way will have noticed that the interior sides of a flask in which they have for some time shaken silver chloride produced by successive precipitation, becomes covered with a kind of varnish of chloride, appears greasy, and so loses its transparency. To obviate this inconvenience when it occurs, I remove, by means of a pipette, a portion of the liquid after it has been agitated and become limpid by standing sufficiently, and transfer it to a bottle having parallel glass sides, and ascertain in this second bottle the presence of silver or salt in excess. The liquid in this bottle was always added to the first whenever it was found necessary to continue the operation.

'The assay presents another difficulty which may lead one greatly into error when not forewarned of it.

'A liquid from which almost all the silver has been precipitated by a saline solution, but which still contains between 1 and 2 milligrammes of silver per litre, is precipitated equally upon the addition of a decimal solution of silver or of salt. In this case, however, there is a very evident difference in the resulting turbidity. The precipitate occasioned by the decimal salt solution in the assay containing 1 or 2 milligrammes of silver in the state of nitrate is always opaque, yellow, and brilliant; whilst the precipitate formed upon the addition of silver nitrate to the same liquid is whitish and translucent. I account for this anomaly by the slight solubility of silver chloride in the alkaline nitrate in solution, and which precipitates in the presence of a silver solution richer than itself. I have, notwithstanding, always added decimal salt solution until precipitation ceases.

'Such is the method of assay which I have adopted for all my estimations by means of double decomposition.'

In a note published subsequently to the above researches, Professor Stas shows how one of the difficulties in the wet assay of silver can be avoided. He says that the Gay-Lussac process is open, under certain conditions, to a source of error arising from the solubility of silver chloride in the very liquid to which its origin is due. This solution, whatever its mode of production may be, is precipitated equally by a decimal solution of silver and by hydrochloric acid or an

alkaline chloride. The extent to which this precipitation ensues is uncertain. At the ordinary temperature there may be a variation of from 1 to $\frac{1}{1000}$ in 100 c.c. of the liquid. Practically, it is quite possible, whilst preserving the simplicity of the wet method of assay, to substitute a bromide or hydrobromic acid for a chloride or hydrochloric acid. This absolutely removes those anomalies which have been observed to be attendant on the use of a chloride or hydrochloric acid.

Professor J. Volhard proceeds as follows:—The alkaline sulphocyanides produce in silver salts a curdy precipitate as insoluble in water as silver chloride. The red solution of ferric sulphocyanide produces the same precipitate, and is decoloured at the same time. If potassium or ammonium sulphocyanide is added to the solution of a silver salt mixed with a ferric salt, a red colouration appears, which is immediately decolourised, and does not become permanent until all the silver is precipitated. This indication is extremely sensitive, and the amount of silver is easily deducted from the quantity of sulphocyanide solution consumed in producing a permanent colouration if the strength of the sulphocyanide is known. This process is much more sensitive than that by Mohr, who employs potassium chromate as indicator, and can be used for the estimation of all bodies which are completely precipitated by silver nitrate from an acid solution. It is merely requisite to add silver nitrate in excess, and estimate the excess of silver remaining after precipitation. To prepare the standard solution of ammonium sulphocyanide—a salt too hygroscopic to be weighed directly—we dissolve about 8 grammes in a litre of water. On the other hand, 10 grammes of fine silver (or 10·8 if the solution is to correspond to the atomic weight) is dissolved in nitric acid and diluted with water to 1000 c.c. To 10 c.c. of this solution add 5 c.c. of ferric sulphate (at 50 grammes ferric oxide per litre), and dilute with 150 to 200 c.c. of water. The sulphocyanide solution is then dropped in with a burette till a permanent red colouration appears. If *e.g.* 9·6 of the sulphocyanide have been required, 960 c.c. of this solution are then diluted to make up 1 litre, when each c.c. will correspond to 10 milligrammes of silver. To assay an alloy of silver 1 gramme is dissolved in nitric acid the solution evaporated in the water-bath, 5 c.c. of ferric sulphate and 200 c.c. of water added, and the sulphocyanide run in. Every $\frac{1}{10}$ of a c.c. used expresses $\frac{1}{1000}$ of silver. The presence of copper within certain limits is without influence. If it amounts to 80 per cent. the precise point of saturation is difficult to seize, either because the blue colour masks the red colouration, or because the cupric solution has an action upon the sulphocyanide. It will be necessary to ascertain if the sulphocyanide undergoes any change in keeping, and if the presence of certain metals renders the result doubtful. Finally, this method requires simplifying for alloys rich in copper and poor in silver.

This simplification may be found, perhaps, in the following reaction : When to a mixed solution of copper and silver potassium ferrocyanide is added, the brown precipitate of copper ferrocyanide does not appear till all the silver has been thrown down.

Separation of Silver Chloride and Iodide.

Silver chloride, when treated with ammonium sulphocyanide in an ammoniacal liquid, is readily and completely converted into silver sulphocyanide, while silver iodide remains untouched.

Cyanogen.—Silver cyanide is converted into sulphocyanide by hydrosulphocyanic acid so rapidly, that dissolved silver cannot be titrated with sulphocyanide solution in presence of silver cyanide. But if the silver cyanide be precipitated from a given quantity of prussic acid by an excess of silver solution, there is no difficulty in titrating the excess of silver in the filter with sulphocyanide solution.

Extraction of Silver from Burnt Pyrites.

In the manufacture of sulphuric acid, iron and copper pyrites are burnt in kilns supplied with a limited amount of air, the products of combustion being thence conducted into leaden chambers, as in the case of vitriol manufactured from ordinary brimstone.

The resulting residue, or 'burnt ore,' was formerly to a large extent smelted for copper, and from the great amounts of iron oxide present, acted as a valuable flux for the more siliceous ores of that metal. It may be taken as containing on the average about 4 per cent. of copper and 18 dwts. of silver to the ton.

For several years past a large proportion of the burnt ore produced in the various chemical works of this country has been worked by what is known as 'the wet process of extraction.'

By this process the burnt ore is first finely ground and sifted, and subsequently roasted with common salt until, by the oxidation of the metallic sulphides present, a portion of alkaline salt is converted into sodium sulphate, whilst the copper is, on the contrary, transformed into a soluble chloride. The copper salt is subsequently removed by repeated washings, and the copper precipitated by iron in the metallic state. It has long been known to those engaged in this business that the copper precipitate produced not only contains a notable quantity of silver but also distinct traces of gold. No attempt, however, to separate the precious metals, and to turn them to profitable account, had been made until Mr. F. Claudet patented a process for the separation of silver from ordinary copper liquors by the addition of a soluble iodide.

The amount of silver present in burnt ore seldom exceeds 18 dwts. per ton ; but, as the whole of this is never obtained in solution, it follows that, dealing with such minute quantities, in order to obtain

satisfactory commercial results, the process employed should be both cheap and expeditious.

The vats, in which the burnt ore which has been roasted with salt is lixiviated, generally receive some 8 or 9 successive washings with either water or with water acidulated by hydrochloric acid, and of these the first three only contain a sufficient amount of silver to be worth working. For the purpose of removing the soluble salts from the ground and washed ore, hot water is employed, and as a large proportion of the sodium chloride used remains undecomposed, it acts as a solvent for the silver chloride produced during the process of furnacing.

The several operations for the extraction of silver are conducted in the following manner; and as the first 3 washings contain nearly 95 per cent. of the total amount of that metal dissolved, these alone are treated.

The liquors are first run into suitable wooden cisterns, each of a capacity of about 2,700 gallons, where they are allowed to settle. The yield of silver per gallon is now ascertained by taking a measured quantity, to which are added hydrochloric acid, potassium iodide, and a solution of lead acetate. The precipitate thus obtained is thrown upon a filter, and, after being dried, is fused with a flux, consisting of a mixture of sodium carbonate, borax, and lamp-black. The resulting argentiferous lead is passed to the cupel, and, from the weight of the button of silver obtained, the amount of that metal in a gallon of the liquor is estimated.

The liquor from the settling-vat is now allowed to flow into another of slightly larger capacity, whilst, at the same time, the exact amount of a soluble iodide necessary to precipitate the silver present is run into it from a graduated tank, together with a quantity of water equal to about $\frac{1}{10}$ the volume of the copper liquor. During the filling of the second tank its contents are constantly stirred, and, when filled, a little lime-water is added, and it is allowed to settle during 48 hours. The supernatant liquors are, after being assayed, run off, and the tank again filled, when the precipitate collected at the bottom is, about once a fortnight, washed into a vessel prepared for its reception.

This precipitate is chiefly composed of lead sulphate, silver iodide, and copper salts, from which the latter are readily removed by washing with water acidulated by hydrochloric acid. Thus freed from copper salts, the precipitate is decomposed by metallic zinc, which completely reduces the silver iodide, and, to a certain extent, also the lead sulphate. The result of this decomposition is—

1st. Zinc iodide, which, after being standardised, is employed in subsequent operations to precipitate further quantities of silver. 2nd. A precipitate rich in silver, and also containing a valuable amount of gold.

The results of nearly six months' experience of this process at the

Widnes Metal Works show that $\frac{1}{2}$ ounce of silver and $1\frac{1}{2}$ grain of gold may be extracted from each ton of ore worked at a total cost, including labour, loss of iodide, &c., of 8*d.* per ton, or 1*s.* 4*d.* per ounce, of silver produced. If from this amount be deducted 6*d.*, the value of the 8 grains of gold contained in each ounce of silver, the cost of production, per ounce of silver, will be reduced to 10*d.*, and the expense of working a ton of ore to 5*d.* This leaves a profit of about 2*s.* on each ton of ore worked.

The value of the precious metals extracted from each ton of ore treated is certainly not large, as the amount originally contained is very small. With richer ores, however, more satisfactory results would be obtained; but when it is stated that some of the copper extraction works operate on 80,000 tons of ore annually, it becomes evident that a profit of 2*s.* per ton is a most important consideration in a business in which competition has rendered care and economy absolutely necessary.

Assay of Silver Ores.

See Separation of Lead from Silver.

For the detection of alkalies in silver nitrate M. Stolba dissolves the salt in the smallest possible quantity of water; the liquid is filtered and hydrofluosilicic acid is added drop by drop. If this produces a turbidity, an alkaline salt is present. If the liquid remains limpid, it is mixed with an equal volume of alcohol, which will precipitate the slightest traces of alkali if present.

MERCURY.

Test for Mercurial Vapours.—M. Merget recommends paper steeped in the ammoniacal solution of silver nitrate or palladium chloride, as reagents for mercurial vapours much more sensitive than gold foil. This test-paper is very sensitive, a slip of sheet-copper plunged into a liquid containing one part of mercury in 10,000 remained bright after immersion, but if exposed to the ammoniacal silver nitrate-paper it occasioned a characteristic black spot. He finds that, even when solidified, mercury emits vapours in appreciable quantity.

Estimation of Mercury in the Metallic State.

In estimating mercury by distillation it is necessary, especially if the metal is in the state of chloride or sulphide, to take certain precautions, without which a portion of the sulphide or chloride would volatilise without decomposition. H. Rose gives the following directions for carrying out the operation:—Introduce into a glass tube capable of resisting fusion, closed at one end, and measuring from 85 to 50 centimetres in length, a column of sodium bicarbonate, then one of quicklime, and then a well-blended mixture of the mercurial compound and quicklime, and, finally, a column of quicklime. The

open end of the tube is drawn out and bent round so as to enter a small flask containing water. The tube is heated as if for an organic analysis, commencing at the open end and finishing with the sodium bicarbonate. The operation ended, cut the bent end of the tube, collect all the mercury in the flask, dry with paper, and afterwards over sulphuric acid, and then weigh it.

The quicklime must not be replaced by lime hydrate. That would occasion all the inconvenience of an analysis of a sulphuretted combination of mercury. The water, acting on the calcium sulphide, would form sulphuretted hydrogen, which, by dissolving in the water of the receiver, would, in time, transform a portion of the reduced mercury into sulphide. It is even advisable in this case to replace the sodium bicarbonate by magnesium carbonate.

Combinations containing mercury iodide are not entirely decomposed when treated as above. Biniodide and protoiodide are condensed in the extremity of the tube simultaneously with the metallic mercury.

To analyse these combinations recourse must be had to metallic copper, the operation being similar to that with quicklime.

Assay of Quicksilver Ores.

The following method, which is suitable for cinnabar, mercuriferous fahlerz, &c., is proposed by A. Eschka. The ore should be weighed in a balance turning with 1 milligramme. The quantity of ore for the assay varies according to its richness, as follows :—

Ore containing up to	1 per cent.	.	.	.	10 grammes
"	"	1	"	10	"
"	"	10	"	30	"
"	"	over 30	"	.	1 gramme

The ore is introduced into a porcelain crucible the edge of which has been ground flat, and mixed with about half its weight of clean iron filings by means of a glass rod, and is then evenly covered with a layer of iron filings about $\frac{1}{4}$ to $\frac{3}{8}$ inch thick. A concave cover, made of fine gold, about 2 inches in diameter and 12 to 15 grammes in weight, is now placed on the crucible after having been carefully weighed; the concavity is filled with distilled water, and the crucible placed on a triangle and heated for 10 minutes by a Bunsen burner or Argand spirit-lamp, during which time the mercury is volatilised and deposits itself on the gold. The gold cover is then removed, the water poured off, and the mirror of mercury on the convex side washed with alcohol from a wash-bottle. After being dried in the water-bath the cover is allowed to cool thoroughly, and is then weighed in a balance turning with $\frac{1}{4}$ a milligramme with 50 grammes in the pan. The increase of weight gives the quantity of quicksilver in the ore. During the weighing the cover is placed on an empty porcelain crucible. The quicksilver is then driven off by heating the cover gently in the flame of a Bunsen-burner or a spirit-lamp, in a place where there is a good

draught, and the empty crucible and cover are subjected to a second weighing as a check. In order that the assay should succeed, the following conditions must be fulfilled. The cover must fit closely, so as to avoid loss of quicksilver, and must be deep enough to hold a sufficient quantity of water to keep it cool. The iron filings must be free from grease, which would prevent the proper formation of the mirror; the washing with alcohol must not be omitted, as it removes all the bituminous substances which spoil the mirror and assist the drying. It must then be dried in a water-bath for 2 or 3 minutes; cooled in the desiccator, and weighed when quite cold. When assaying rich ores the alcohol used in washing the cover must be collected, as it may contain a little amalgam; it must be poured into the concavity of the cover, which will take up any little globules of quicksilver. The most exact results are obtained in the case of ores containing less than 10 per cent.

Smithson's Gold-tin Battery for the Detection of Mercury.

J. Lefort states that the gold-tin element proposed by Smithson for the detection of traces of mercury has been subjected by Orfila to a criticism which is only in part well founded. If the apparatus is left for a considerable time in a liquid supposed to be mercurial, a small quantity of tin may dissolve and be deposited upon the leaf of gold, so that it is turned white even in the absence of mercury. So far, therefore, the experiment may lead to a doubtful or erroneous result, but as tin is not volatile it is merely requisite to heat the slip of gold in a narrow tube, in order to drive away the adhering deposit, and then to act upon the metallic sublimate with vapour of iodine, thus forming mercuric iodide of a more or less decided red colour. If the mixture operated upon contains merely mercury, the operation thus described leaves no doubt as to the sensibility and the exactness of the process. But here the trustworthiness of the Smithson battery ceases, as it does not confine its action to the reduction of mercurial salts. The search for mercury in mineral waters has enabled the author to observe that arsenious and arsenic acids are easily reduced by the Smithson battery. As metallic arsenic is volatile, like mercury, and forms with iodine a compound of a red colour, more or less comparable to that of mercuric iodide, it follows that these two elements may be respectively confounded, especially when the red sublimate is obtained only in microscopic quantities. Hence, it appears that the arsenic oxides are readily decomposed by metals under the influence even of a very feeble electric current. Thus a slip of copper immersed in a solution containing $\frac{1}{1000}$ of arsenic acid does not change its appearance, but if hydrochloric acid is added, and especially a little common salt, metallic arsenic is deposited upon the copper. This fact ought not to be forgotten when the very general presence of mercury in mineral waters is admitted on the faith of imperfect analyses.

Electrolytic Estimation of Mercury.

F. W. Clarke puts a solution of mercuric chloride, slightly acidulated with sulphuric acid, in a platinum capsule connected with the zinc pole of a Bunsen bichromate battery of 6 elements. The wire at the end of the carbon pole terminates in a thin slip of platinum foil, which dips into the solution. At first mercurous chloride is deposited, which gradually takes the metallic state, and after the lapse of an hour there is nothing in the capsule but globules of pure mercury, covered with a solution in which ammonia occasions not the slightest turbidity. This liquid is withdrawn with a pipette, and water poured in its place a time or two before separating the connection with the battery. The liquid is then decanted off and the mercury washed first with water, then with alcohol, and lastly with ether, and is then dried under the air-pump.

Estimation of Mercury in the Form of Protochloride.

M. de Bonsdorff proposes to precipitate mercury as protochloride by alkaline formiates. This method may lead to completely erroneous results, as alkaline formiates do not invariably reduce mercury bichloride. The affinity of mercuric chloride for alkaline chlorides is so great that when these bodies are present the ordinary reactions of mercury are not produced. When a liquid contains much hydrochloric acid, an alkali does not precipitate mercury oxide from it. Sulphuric and nitric acids have the same effect. Such a mercuric solution, containing a large excess of potash, is not precipitated by ammonium sulphide unless the base has been previously supersaturated with an acid.

The best method for estimating mercury is to precipitate it in the state of protochloride by phosphorous acid. When the liquid contains free hydrochloric acid, the temperature may be raised to 60° C., without the mercury protochloride being reduced to the metallic state by phosphorous acid. The precipitated protochloride is not immediately formed in very weak liquids; it is necessary to leave the mixture undisturbed for 12 hours. The chloride deposits itself readily, especially when the liquid is sufficiently acid. The precipitate is to be collected on a filter, washed with cold, or even hot water, and dried at 100°. This process is very applicable to cases where the liquid contains much nitric acid. Only the solution must then be diluted with a sufficient quantity of water.

Separation of Mercury (Persalts) from Silver.

Add a sufficient quantity of hydrochloric acid to the diluted solution. After the deposition of silver chloride, decant the supernatant liquid; then heat the chloride precipitate with a small quantity of

nitric acid, add some water and a few drops of hydrochloric acid, and then filter. Precipitate the mercury from the filtered liquid by phosphorous acid, according to Rose's process, already described. ‡

Separation of Mercury from Zinc.

This separation may be readily effected by precipitating the mercury in the state of protochloride by phosphorous acid, in the presence of free hydrochloric acid. The process may be carried out as previously described.

COPPER.

Detection of Traces of Copper.

According to Drs. Endemann and Prochazka, if to a dilute solution of a copper salt concentrated hydrobromic acid is added, a dark brownish or violet colour is at once produced.

This reaction is so delicate that $\frac{1}{100}$ of a milligramme of copper can be detected with certainty. One drop of a solution containing this small quantity of copper is brought on a watch-glass, one drop of hydrobromic acid is added, and the solution is then allowed to evaporate slowly by standing the glass on a warm place. When the whole has been concentrated to about one drop, this will distinctly show a rose-red colour. The colour then produced is about 3 or 4 times as distinct as the one which is obtained by the addition of potassium ferrocyanide. Of other metals which are examined in this direction, they find that only iron is apt to interfere with this reaction, and then only when it is present in considerable quantity.

This reaction may also be utilised as a colorimetric test for the quantitative estimation of small quantities of copper.

The following is a very delicate test for copper :—A zinc-platinum element is formed of two thin wires, which is then placed in the solution to be tested. Should there be much copper present, almost immediately the platinum becomes covered with a blackish deposit; but if the solution is very dilute it is necessary to leave the wires in for some hours, when probably the platinum will be only slightly, if at all, coloured. The platinum wire is now removed, washed with water, and exposed, without previous drying, for a few moments to the action of hydrobromic acid and bromine vapour, obtained by heating a small quantity of potassium bromide with strong sulphuric acid. The deposit becomes deep violet. The colour may be more easily recognised by rubbing the platinum wire upon a piece of porcelain.

Mr. R. C. Woodcock has experimented on the delicacy of this reaction. He dissolves metallic copper in nitric acid, and then dilutes the solution until 8 c.c. contains 0.0000008 gramme of copper; 8 c.c. are then taken, and a drop of dilute hydrochloric acid added, the zinc-

platinum element placed in the solution, and left for 19 hours, after which time the copper can just be detected by applying the above test.

Precipitation of Metallic Copper in Quantitative Analyses.

The estimation of copper in the state of oxide, simple as the operation appears, is, nevertheless, always more or less faulty, and the results are not sufficiently exact. After the copper oxide has been precipitated by potash and calcined, the filter in which the oxide is retained, and from which it is impossible to detach it, reduces a portion of the copper. The metal must therefore be reoxidised. But calcining in a vessel open to the air, or even in a current of pure oxygen, will not completely re-form the oxide. The oxygenation of the metal remains imperfect, however long the reaction may be continued. Recourse must now be had to nitric acid, whose oxidising action is perfect; but another inconvenience then arises. When the copper nitrate is decomposed, some of the oxide is carried off in the stream of nitrous vapours. This phenomenon is shown very visibly by experimenting in a small glass flask holding 100 c.c., with a neck 7 or 8 centimetres long. However carefully the decomposition of the nitrate may be conducted, the interior of the flask and its neck are entirely covered with an impalpable powder of cupric oxide, some even escaping from the flask in appreciable quantities.

On very carefully experimenting in a comparatively large and well-closed platinum crucible there is a notable loss. Thus, according to some experiments of MM. Millon and Commaille, 1.8805 gramme of pure copper gave but 1.6605 gramme of oxide instead of 1.6675 gramme.

To obviate these difficulties copper should be estimated in the metallic state. The oxide is precipitated by potash, and the precipitate, washed with hot water and dried, is burnt, with the filter, in a large platinum capsule. The residue of this calcination does not adhere to the sides of the capsule. It is placed in a platinum vessel, where it is reduced by a current of pure hydrogen.

According to M. Th. Weyl, copper reduced in hydrogen retains a certain quantity of this gas, falsifying the results of the analysis. This inconvenience may be avoided by reducing copper oxide by the vapours of formic acid.

Precipitation of Copper as Sulphide.

This would be an excellent form in which to estimate copper were it not that, on the ignition previous to weighing it, the sulphide oxidises and loses sulphur, the result being a mixture of disulphide, sulphate, and oxide. David Forbes has shown that this difficulty can be got over in a similar manner as in the case of nickel (see page 246). The weight of sulphur in the copper sulphide and of oxygen in the oxide

being identical, a mixture of sulphide and oxide in varying proportions may be weighed and calculated as if it were pure oxide or pure sulphide. It is only necessary, therefore, to remove the small quantity of sulphuric acid in the ignited copper sulphide. This is effected by adding a small amount of ammonium carbonate to the incinerated sulphide as soon as it is cold, and then carefully heating until all ammoniacal salts are expelled. Some attention must be paid to the details of the operation, as the copper sulphide, especially in cases where free sulphur has been precipitated along with it, is very apt to aggregate together or even fuse during the incineration (if this is not very carefully conducted), and, consequently, it is less easily acted on by the air during incineration; this must be avoided, and the oxide should also not be allowed to absorb hygrometric moisture before or during weighing.

Instead of precipitating copper from solution, in presence of other metals, with zinc, its separation is more conveniently effected by means of an electric current. The slightly acid solution of the copper sulphates and other metals is contained in a platinum crucible which forms the negative pole of an electric current from two of Bunsen's cells; the positive pole terminates in platinum foil, and passes through a perforation in a watch-glass which covers the crucible, dipping into the liquid. The copper separates in a perfectly pure state, and the reduction is accomplished in 3 or 4 hours. The intensity of current, concentration of solution, temperature, and amount of free acid may vary within wide limits without impairing the accuracy of the result.

Estimation of Copper as Sulphocyanide.

M. A. Guyard employs a reagent obtained by dissolving in water equal weights of ammonium sulphocyanide and bisulphite. This mixture keeps well, and can be used several months after its preparation, providing it is not left exposed to the air for any length of time; but, should a slight alteration take place in its composition, this would be of no consequence.

A mixture of equal weights of potassium sulphocyanide and sodium bisulphite answers equally well; in fact, it keeps still better than the former mixture, and the only objection to its use is its being composed of fixed salts.

The important property of this reagent consists in forming, in solutions of copper acidulated with hydrochloric acid, an abundant white precipitate of copper sulphocyanide which is completely insoluble.

The only precaution to take to ascertain the presence of copper in a solution is to neutralise any nitric acid which might be present with an excess of ammonia, and then to acidulate the solution with a slight excess of hydrochloric acid.

When the white precipitate of copper subsulphocyanide is thoroughly washed—and this is the case when free from chlorides which adhere

more strongly to the precipitate than sulphocyanides—and when the precipitate is thoroughly dried it contains 52·80 per cent. of copper.

As in chloride solutions, the only metal precipitated by the reagent is copper; it affords easy means of separating this metal from all others, and of estimating it with promptitude and with the greatest accuracy. The drying of the precipitate being the longest part of the operation, whenever it is required to make a rapid estimation the process can be modified as follows:—The washed copper sulphocyanide is detached while wet from the filter; the filter is burnt, and its ashes are mixed with the precipitate, which is digested for some time with an excess of ammonium sulphide. By this means copper sulphide is obtained. It is filtered and thoroughly washed; it is then dried very rapidly in a small porcelain crucible and calcined. This being done a little excess of pure flour of sulphur is thrown in the crucible, which is then carefully covered, and all the sulphur is driven off at a low red heat. After cooling, the residue of copper sulphide presents the constant formula Cu_2S , and it contains exactly $\frac{2}{3}$ of its weight of copper.

Estimation of Copper in Bar Copper and in Native Copper.

Twenty grains of the metal are dissolved in nitric acid, and if the solution is quite clear, the copper is estimated exactly as in the former example. If, on the contrary, a precipitate of antimony or tin oxides is manifest in the liquor, it should be dissolved by adding a little hydrochloric acid, or a fresh lot of metal should be dissolved in aqua regia. This being done, the estimation of copper is proceeded with exactly as previously stated.

For the complete analysis 100 grains are dissolved in nitric acid or in aqua regia. The solution, supersaturated with ammonia, is re-acidulated with a slight excess of hydrochloric acid, and the liquid is then added. With the precaution already indicated, and in general when the precipitation is complete, the supernatant liquid assumes a pink or red colour due to iron sulphocyanide. The liquid is then filtered on a double filter (this precaution is useful because copper sulphocyanide is apt to pass through single filters), and the precipitate is well washed. The liquid, mixed with a little more hydrochloric acid, is boiled until no smell of sulphurous acid from the reagent can be detected; it is then submitted to analysis.

Lead, arsenic, and antimony will generally be found. Even coppers leaving no residue in nitric acid contain antimony which can be detected and estimated when separated in this way. The same remark applies to tin, which exists more often than might be supposed. Bismuth, nickel, and zinc are three metals which exist very frequently also in copper. Cobalt is found pretty often too, and silver and iron are nearly always present.

Sulphur, which exists frequently, must be estimated in a special operation.

Estimation of Copper in Brass, Bronze, and German Silver.

Quantities of the alloys, varying from 20 to 50 grains, should be dissolved for the estimation of their chief constituents, and no less than 100 grains should be employed for the estimation of the smaller quantities of foreign metals. The proceedings are identical with those indicated in former examples.

In bronzes, it would be advisable to dissolve the alloy in aqua regia, and proceed first to the separation of copper.

With these alloys the copper reagent proves invaluable, not only as affording means of estimating with facility and accuracy the composition of important alloys, but also as enabling the chemist to estimate the very important question of the cause or causes of brittleness in those alloys.

Estimation of Copper in Pyrites and other Copper Ores, and in Slags.

The reagent proves much less useful and necessary in the analyses of these minerals and slags than in those of the former products, for the reason that ordinary methods answer well when applied to them. Indeed, it is not advisable to use the reagent at first to effect the separation of copper, unless this metal exists in large quantity, and is alone to be estimated. However, if uniformity in the estimation of copper was an object, no objections would be raised against using the reagent, which separate the copper with equal perfection, whatever substances accompany it. But for analytical purposes it would be best to precipitate by sulphuretted hydrogen, copper, and the group of metals which are precipitated with it, and thus to separate them from the large proportions of iron and of earthy matters which may be present.

The precipitated sulphides being redissolved in nitric acid or in aqua regia, this solution can be submitted to analysis, and, in most cases, the reagent can be employed with advantage in this part of the operation, and if copper is the most abundant metal of all, it will prove as useful as ever. If, on the contrary, copper formed only a small fraction, it would be best not to use the reagent at all, but to apply the ordinary methods of separation.

Some pyrites and certain earthy minerals contain about equal proportions of bismuth and copper. In these instances it is best to separate bismuth first, to avoid all possibility of this metal being precipitated by water and mixed up with copper. The same remark applies to cases where antimony is present in large proportions.

As a general rule, when a metal, such as lead, silver, antimony, or bismuth, exists in large proportions, and when this metal can be easily separated from copper, it is best and safest to effect its separation at once.

There are instances in which the separation of copper is not only difficult but imperfect with ordinary methods. Such is the case when copper exists in a liquid with palladium, vanadium, molybdenum, and cadmium. In these instances no better means of separation can be resorted to than to use the mixed sulphocyanide and bisulphite reagent, which effects all these separations with the greatest perfection.

Volumetric Estimation of Copper.

Mohr's method of estimating copper, by adding a standard solution of potassium cyanide to an ammoniacal solution of copper, Herr Fleck says, offers two objections; the quantity of cyanide necessary to destroy the blue colour varies according to the quantity of ammonia the liquid contains, and at the end of the operation it is difficult to tell the exact moment at which the blue colour disappears. To remedy these inconveniences, Herr Fleck proposes to dissolve the copper compound in ammonium carbonate instead of ammonia. He shows that an excess of this salt does not interfere with the reaction. In the second place, he adds a drop of potassium ferrocyanide to the blue liquor, and then at the moment the cupro-ammoniacal compound is destroyed the liquid becomes red.

Estimation of Copper with Potassium Ferrocyanide.—When the copper ore, after having been acted upon by acids, is treated with excess of ammonia in order to precipitate the iron oxide, that substance invariably retains larger or smaller quantities of the copper oxide. The quantity thereof so retained varies according to the larger or smaller quantity of copper contained in the ores. It is hence necessary to repeat the treatment with ammonia at least twice, sometimes even three and four times, in order to obtain a complete separation of copper from iron.

In order to obviate the loss of time which is caused by these operations, M. Maurizio Galetti, Chief Assayer and Chemist to the Royal Assay Office at Genoa, proposes to convert into acetate the small quantity of copper oxide which accompanies the precipitate of iron oxide. This can be effected by two different methods, dependent on the fact whether the iron oxide is removed by filtration (previous to the use of standard solution of potassium ferrocyanide), or is left in the ammoniacal liquid. The operations are conducted as follows:—

1. Suppose a copper pyrites be submitted to analysis. Take 1 gramme of the previously very carefully pulverised and dried ore. Treat it first with concentrated nitric acid, boiling to incipient dryness in order thereby to free the sulphur from any small particles of ore which are at first taken up by it. Add 10 c.c. of hydrochloric acid, boil down to about half that bulk, dilute with distilled water, and next add ammonia in large excess; boil the fluid, and next add acetic acid until the liquid assumes an emerald-green colour. After the liquid

has been well stirred, boil again for about 2 minutes ; and again add ammonia in excess. The liquid is then poured out of the flask into a suitable glass vessel, and the flask is rinsed out with a sufficient quantity of distilled water to bring the bulk of the fluid up to $\frac{1}{2}$ litre. This having been done, the fluid is very cautiously and gradually acidified with dilute acetic acid. Any considerable excess of this acid should be avoided. As soon as the basic iron acetate has subsided, the precipitation of the copper by means of the standard solution of potassium ferrocyanide is proceeded with.

Since the copper oxide, which might have adhered to the iron oxide, has been converted, by the process just described, into a soluble salt, it cannot fail to be completely precipitated by the potassium ferrocyanide solution. When an estimation of copper has to be made in ores which are rather poor (that is to say, contain less than 6 per cent. of copper), it is preferable to add to the nitric acid solution 0.1 gramme of pure copper, which quantity has to be deducted afterwards from the results obtained. This precaution is required in order to prevent the presence of a large quantity of iron oxide from vitiating the results of analysis of poor ores. When ores contain up to 12 per cent. of copper, a quantity of 1 gramme of the ore should be taken ; but for richer ores 0.5 gramme is sufficient. It is always advisable to make a control analysis with pure copper at the same time while testing the ores.

2. The second modification is carried out in the following manner :

After the second addition of ammonia to the liquid, it is filtered, and the precipitate is washed with a dilute and boiling solution of acid ammonium acetate. This solution is prepared by saturating 20 grammes of pure acetic acid with ammonia, and adding thereto 15 grammes of pure acetic acid in 585 grammes of water. When the washing of the iron oxide is carefully done, the copper salt, which tenaciously adheres to the iron oxide, is entirely removed therefrom ; but it will require about 400 grammes of the fluid, the preparation of which has just been described.

The normal solution of copper for standardising the potassium ferrocyanide should be prepared as follows :—

0.2 gramme of pure copper is dissolved in nitric acid ; excess of ammonia is added ; the fluid next acidified with acetic acid, then diluted with 400 grammes of acid ammonium acetate, and the whole brought up to 500 grammes. To this solution 20 c.c. of the standard solution of potassium ferrocyanide are added, when the liquid should not contain any excess of either copper or of ferrocyanide.

The standard solution of potassium ferrocyanide to be used for the estimation of copper is made by dissolving 50.225 grammes of ferrocyanide in as much distilled water as will suffice to make the solution weigh exactly 1 kilogramme.

If the copper ores contain zinc, nickel, and cobalt, the copper should be first separated from these metals, either by precipitating the copper

from its solution by means of zinc, or as copper sulphide by means of sodium thiosulphate.

Estimation of Copper with Sodium Sulphide.—An ammoniacal solution containing $\frac{1}{1000}$ of copper reacts distinctly on moist, recently precipitated zinc sulphide—the zinc dissolving, while the copper is precipitated in the form of sulphide. Zinc sulphide decomposes instantly in a hot ammoniacal solution of copper.

Starting from this reaction, Dr. C. Kunsel proposes the following volumetrical method for the estimation of copper :—

He prepares pure sodium sulphide by saturating a solution of caustic soda free from carbonate, with sulphuretted hydrogen, and driving off the excess of the gas. The solution is then diluted so that a cubic centimetre precipitates a centigramme of copper.

A known weight of pure copper is dissolved in nitric acid, the solution supersaturated with ammonia, diluted, and heated to boiling. The solution of sodium sulphide is then added to the hot solution of copper, stirring continually until a drop of the mixed solutions no longer colours zinc sulphide brown. Zinc sulphide for indicating the complete precipitation of the copper is prepared in the following way :—Zinc is dissolved in hydrochloric acid, the solution is supersaturated with ammonia and is then boiled with a little zinc sulphide to remove the lead which is always present in commercial zinc. The ammoniacal solution of zinc, now free from lead, is filtered and decomposed with sodium sulphide, a small quantity of zinc being allowed to remain in solution. The moist zinc sulphide, with excess of zinc solution, is then spread evenly upon filter-paper several layers thick. When the paper has absorbed most of the solution the moist white layer of zinc sulphide is ready for use.

The ore or alloy, free from arsenic, is dissolved in hydrochloric acid with the addition of some nitric acid, and, when necessary, is evaporated to dryness, the deposit dissolved in hot water, and filtered to separate silica. Any iron may be removed from the mixed chlorides by the addition of ammonia. The solution freed from iron is then rendered strongly ammoniacal, heated to boiling, and the standard solution of sodium sulphide added (with continual shaking) until a drop of the mixed solutions no longer acts on zinc sulphide, *i.e.* until all the copper is precipitated. The number of cubic centimetres of the standard solution is then read off and the amount of copper calculated.

The following volumetric methods may be occasionally useful. M. F. Weil bases a method on the following principles :—

(1.) That with an excess of free hydrochloric acid, and at boiling heat, the presence even of the smallest quantity of copper chloride may be detected by the greenish-yellow colour of the solution, this colour being the stronger and more prominent the more free hydrochloric acid prevails.

(2.) The aqueous solutions of copper chloride, which contain free

hydrochloric acid, become, while boiling, upon the addition of tin protochloride, instantaneously converted into colourless solutions of copper protochloride. The reaction is quite finished as soon as, by the addition, drop by drop, of the tin protochloride, the green colour of the copper perchloride is changed to the colourless copper protochloride. Even a single drop of tin protochloride added in excess can be readily detected by the addition of a single drop of a solution of corrosive sublimate, which produces a precipitate of white mercury protochloride. It is clear, therefore, that the quantity of the solution of tin protochloride, which is required for the perfect decolouration of the copper solution, will indicate the quantity of the copper present in the solution. If it contains iron along with the copper, the iron will have to be estimated in a separate portion of the solution by means of potassium permanganate; while, in the estimation of the copper, the quantity of tin protochloride equivalent to and converted by the iron into iron perchloride has to be deducted.

I. Preparation and Keeping of the Solution of Tin Protochloride.—Take about 6 grammes of tin foil (this material ought first to be tested for its purity), dissolve in 200 c.c. of pure hydrochloric acid at a boiling heat, and with the addition of some pieces of platinum wire; the tin solution thus obtained is diluted to 1000 c.c. by the addition of distilled water, and is poured into a wide-mouthed glass bottle, after which the solution is covered over with a layer of petroleum. This bottle is provided with a glass syphon-tube and stop-cock attached, and also with a funnel-tube for replenishing the solution. This solution, although kept under petroleum, and thereby protected from the action of the air, only keeps sufficiently steady and unaltered for a single day, so that the liquid has to be tested and accurately titrated every morning, before using it for the estimation of copper in solutions wherein the quantity of that metal is unknown.

II. Titration of Tin Protochloride for Pure Copper.—Take chemically pure, recrystallised, pulverised copper sulphate, deprived of adhering moisture by pressing between filtering-paper; weigh off 7.867 grammes (equal to 2 grammes of pure metallic copper), dissolve in distilled water, and dilute to 500 c.c.; keep this solution as a normal solution of copper in a glass-stoppered bottle. Take of this solution by means of a pipette, 25 c.c. (equal to 0.1 gramme of pure copper), pour this quantity into a flask capable of containing 100 c.c.; add 5 c.c. of pure hydrochloric acid, which causes the blue fluid to become deep green; and next boil the liquid upon a sand-bath; then take a burette, divided into c.c. and $\frac{1}{10}$ c.c., fill it with the solution of tin protochloride up to zero, and immediately after pour rapidly into the boiling copper solution sufficient of the tin salt to cause the same to become very nearly decolourised. After this the tin solution is added, drop by drop, until the copper solution is as clear and colourless as distilled water; as soon as this point has been reached, add with a

pipette again 5 c.c. of pure hydrochloric acid, and, if by this addition the slightest green colouration is produced, tin protochloride is added, drop by drop, until the decolouration is complete; after this, the quantity of tin solution employed is read off. If it is desired to make sure that the end of the reaction is properly reached (a precaution which is quite unnecessary if 10 c.c. of hydrochloric acid have been added) 1 c.c. of the colourless solution is taken, by means of a pipette, and poured into a test-tube; this tube is placed in cold water to promote the rapid cooling of the contents; and, after cooling, there is added to the solution one drop of a concentrated aqueous solution of mercury chloride. If this does not bring about a turbidity or precipitate, it is best to add to the contents of the flask another drop of tin protochloride solution; this having been done, the testing of the contents of the flask by means of mercury chloride, as just mentioned, is repeated, and if a turbidity or precipitate ensues, the quantity of tin solution applied is read off, care being taken to deduct therefrom $\frac{1}{10}$ of a c.c. Every 16.2 c.c. of the tin solution correspond to 0.1 gramme of metallic copper.

III. Titration of any Compound of Copper not containing either Iron or Nickel.—Take 4 grammes of the metal, either reduced to powder or at least cut (not filed) to a convenient size; dissolve in strong nitric acid contained in a long-necked flask; expel the excess of this acid by boiling with excess of sulphuric acid or with hydrochloric acid in case silver is contained in the substance taken for assay; next, water is added, and the bulk of the fluid brought to from 250 to 500 c.c., according to the presumable quantity of copper present, care being taken to mix the liquid thoroughly, and thereby render it uniform throughout. It is not absolutely required to remove by filtration insoluble substances, such as silica, lead sulphate, stannic acid, antimonious acid, silver chloride, and the like, since these substances settle readily to the bottom of the tall cylindrical jar employed for containing the liquid, while the assay is being made. The tin solution is added after the addition, as above stated, of some 5 or 10 c.c. of hydrochloric acid.

IV. Titration of a Compound of Copper which also contains Iron.—The weighing off of the substance, its solution in acid, and the titration of 25 c.c. of the joint solution of the two metals, is performed as described under III., with this difference, that the operation of adding the tin solution is performed with the solution of the metals contained in a flask of a capacity of at least 250 c.c. After the total quantity of tin solution required at the first titration has been noted, the titration of the iron is executed in the following manner:—Some 25 or 50 c.c. of the sulphuric acid solution are diluted with a large quantity of water, and placed in a flask of 250 c.c. capacity; to this liquid, metallic zinc and platinum wire are added, and left in the solution until it is perfectly colourless; the entire quantity of copper,

tin, lead, arsenic, antimony, &c. which might be present is precipitated in the metallic state; the colourless fluid is then decanted, and the iron volumetrically estimated by means of potassium permanganate.

Observation on the Titration of Compounds of Copper containing Iron.—If the operator does not happen to have ready at hand a titrated permanganate solution for the estimation of the iron, the titration of the fluid containing copper and iron can be readily performed in the following manner:—Precipitate, as above mentioned, by the aid of zinc and platinum, all the copper, &c., decant the supernatant fluid, wash the precipitated metal (or metals) with distilled water, and dissolve these in sulphuric acid, and estimate next in 25 c.c. of that solution (after previous addition of from 5 to 10 c.c. of pure hydrochloric acid), by titration with tin perchloride solution, the copper directly without the necessity of estimating the iron at all.

V. Titration of a Compound of Copper which contains Nickel.—Since the green colour of the nickel salts prevents the complete and perfect decolouration, by stannous chloride, of a solution which contains copper and nickel together, titration by means of the tin salt, as described, can be employed, but the end of the reaction must be tested for by the use of the solution of corrosive sublimate. In preference, however, to this, the following method may be employed:—The substance to be tested (about 4 grammes) is dissolved in nitric acid, or, if need be, in nitro-hydrochloric acid; next, the greater part, but not all the acid, is saturated with sodium carbonate; then add, after having diluted the fluid with cold water, an excess of freshly precipitated barium carbonate, to which some ammonium chloride is added, and which together are suspended in water. This milky fluid is thoroughly stirred through the metallic solution; by this proceeding, a precipitate ensues, which contains all the copper as hydrated oxide, and, if present, the iron also as hydrated oxide, while the nickel remains in solution. The precipitate is first washed by decantation, next collected on a filter, thoroughly washed, and, after having been redissolved in hydrochloric acid, titrated as above described. The presence of arsenic or its compounds does not in the least interfere with the process; while, if cobalt happens to be present—which will, however, be only rarely the case—the treatment is the same as for nickel. By a series of test experiments, and by comparison with gravimetical analysis, the process above described is found to be thoroughly reliable and to give accurate results.

For the volumetric estimation of copper, M. P. Casamajor precipitates copper and lead from alkaline solutions by a titrated solution of sodium sulphide. This was the reagent used by Pélouze for the volumetric estimation of copper in a process published some 30 years ago in the *Annales de Chimie et de Physique*. In the process of Pélouze copper is dissolved in a large excess of ammonia, by which

an intensely blue liquid is obtained, and a titrated solution of sodium sulphide is added, until the blue colour disappears.

Instead of using an excess of ammonia, Mr. P. Casamajor uses an alkaline tartrate dissolved in an excess of caustic soda. This liquid is the same which, added to a titrated solution of copper sulphate, forms Fehling's solution. It is prepared by dissolving 178 grammes of Rochelle salt in 480 c.c. of caustic soda of sp. gr. 1.14, and adding water to form 1 litre of solution. This alkaline solution is added to the copper solutions in slight excess of the quantity sufficient to dissolve the copper to a deep blue-coloured liquid, and the porcelain dish is heated so that the liquid is carried to nearly the boiling-point. The titrated solution of sodium sulphide is then added until no turbidity is produced by the addition of 1 drop.

In this manner of proceeding the blue colour of the solution is not taken into account. The dark brown colour which follows the addition of the reagent is the only guide. The first addition of the alkaline sulphide gives rise to an intense black-brown precipitate. As soon as this is formed, the liquid in the dish is thoroughly stirred with a glass rod. This has the effect of agglomerating the copper sulphide into coarse curds, which settle to the bottom of the dish, leaving the liquid clear and almost colourless. If, after settling, the liquid should not be sufficiently clear, it should be vigorously stirred again until the desired effect is obtained. After every addition of sodium sulphide the liquid should be thoroughly agitated until it becomes clear. The degree of turbidity produced is a guide as to the quantity of reagent to use. At the beginning the brown cloud is very intense, and it is useless to await the complete clearing up of the liquid before adding more of the reagent. Towards the end the brown cloud is comparatively slight, and the reagent should be added drop by drop. The liquid in the dish should be stirred so as to clear it up entirely before adding a drop of the reagent.

By thorough stirring the copper sulphide agglomerates in thick heavy curds, which settle rapidly, leaving the surface of the dish very clean, as seen through the clear liquid. On this clean white surface the faintest cloudiness is easily seen. A liquid containing 1 part of copper in 30,000 parts of solution will give a distinct brown turbidity by the addition of 1 drop of the reagent.

Copper can be separated from other metals as sulphocyanide (Rivot's process). The precipitate is heated with nitric acid and redissolved. This solution is afterwards treated by the alkaline tartrate solution, and the copper precipitated as sulphide. Copper may also be precipitated as cuprous oxide by glucose from an alkaline tartrate solution. The cuprous oxide may be dissolved in nitric acid, then alkaline tartrate solution added to obtain a clear blue solution, from which copper may be separated as copper sulphide. This is applicable to testing glucose and cane-sugar.

Dr. T. Carnelley proposes the following colorimetric method for the estimation of small quantities of copper:—The reagent used is the same as in the case of iron, viz. potassium ferrocyanide, which gives a purple-brown colour with very dilute solutions of copper. Of the coloured reactions which copper gives with different reagents, those with sulphuretted hydrogen and potassium ferrocyanide are by far the most delicate, and as a preliminary the comparative values of these two reagents were tested, with the following results, the estimation being made in each case in 150 c.c. of water:—

1. **With Sulphuretted Hydrogen.**—One part of copper produces a colour in $\frac{1}{300000}$ parts of water.

2. **With Potassium Ferrocyanide.**—(a). In acid solutions, the colour produced being earthy brown, 1 part of copper produces a colour in $\frac{1}{100000}$ parts of water. (b). In neutral solutions, the colour being purple-brown, 1 part of copper produces a colour in $\frac{1}{300000}$ parts of water. (c). In neutral solutions containing ammonium nitrate, the colour being purple-brown, 1 part of copper produces a colour in $\frac{1}{300000}$ parts of water.

From the above, it will be seen that of the two reagents sulphuretted hydrogen is the more delicate, except in the latter case, when they are of equal value. But potassium ferrocyanide has a decided advantage over sulphuretted hydrogen in the fact that lead, when not present in too large quantity, does not interfere with the depth of colour obtained, whereas to sulphuretted hydrogen it is, as is well known, very sensitive.

And though iron, if present, would, without special precaution being taken, prevent the determination of copper by means of potassium ferrocyanide, yet by the method as described below the amounts of these metals contained together in a solution can be estimated by this reagent.

As the above results show, ammonium nitrate renders the reaction much more delicate; other salts, as ammonium chloride and potassium nitrate, have likewise the same effect.

The method of analysis consists in the comparison of the purple-brown colours produced by adding to a solution of potassium ferrocyanide, first, a solution of copper of known strength, and secondly, the solution in which the copper is to be determined.

The solutions and materials required are as follows:—

1. **Standard Copper Solution.**—Prepared by dissolving 0.898 gramme of pure crystallised copper sulphate in 1 litre of water; 1 c.c. is then equivalent to 0.1 milligramme copper.

2. **Solution of Ammonium Nitrate.**—Made by dissolving 100 grammes of the salt in 1 litre of water.

3. **Potassium Ferrocyanide Solution.**—Containing 1 part of the salt in 25 parts of water.

4. **Two glass cylinders,** holding rather more than 150 c.c. each,

the point equivalent to that volume being marked on the glass. They must, of course, both be of the same tint, and as nearly colourless as possible.

5. A burette, marked to $\frac{1}{10}$ c.c., for the copper solution; a 5 c.c. pipette for the ammonium nitrate; and a small tube to deliver the potassium ferrocyanide in drops.

The following is the method of analysis:—Five drops of the potassium ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined into 1 of them (A), and both filled up to the mark with distilled water, 5 c.c. of the ammonium nitrate solution added to each, and then the standard copper solution run gradually into (B), till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of cubic centimetres used are then read off. Each cubic centimetre corresponds to 0.1 milligramme of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be estimated must be neutral, for if it contains free acid the latter lessens the depth of colour and changes it from a purple brown to an earthy brown. If it should be acid it is rendered slightly alkaline with ammonia, and the excess of the latter got rid of by boiling. The solution must not be alkaline, as the brown colouration is soluble in ammonia, and decomposed by potash; if it is alkaline from ammonia this is remedied as before by boiling it off; while free potash, should it be present, is neutralised by an acid, and the latter by ammonia.

Within moderate limits the amount of potassium ferrocyanide does not affect the accuracy of the method, as was proved by several experiments; for instance, when $\frac{1}{2}$ c.c. and 2 c.c. of the ferrocyanide were added to the 2 cylinders respectively, water up to the mark, and 5 c.c. of ammonium nitrate to each, then 7 c.c. of the standard copper solution produced in each an equal depth in colour.

The same may be said of the ammonium nitrate, for in one of several trials, all leading to the same result, when there were 5 drops of ferrocyanide in each cylinder, with water up to the mark, and 5 c.c. of ammonium nitrate in one and 15 c.c. in the other, an equal depth of colour was obtained on running into each 7 c.c. of the standard copper solution.

When copper is to be estimated in a solution containing iron, the following is the method of procedure to be adopted:—To the solution a few drops of nitric acid are added in order to oxidise the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present this can be done easily and completely if there is only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid, and reprecipitated by ammonia, filtered, and

washed. The iron precipitate is now free from copper, and in it the iron can be estimated by dissolving in nitric acid, making the solution nearly neutral with ammonia, and estimating the iron by a colorimetric method. The filtrate from the iron precipitate is boiled till all the ammonia is completely driven off, and the copper estimated in the solution so obtained, as already described.

When the solution containing copper is too dilute to give any colouration directly with potassium ferrocyanide, a measured quantity of it must be evaporated to a small bulk, and filtered if necessary, and if it contains iron, also treated as already described.

In the estimation of copper and iron in water, for which the method is especially applicable, a measured quantity is evaporated with a few drops of nitric acid to dryness, ignited to get rid of any organic matter that might colour the liquid, and dissolved in a little boiling water and a drop or two of nitric acid (if it is not all soluble it does not matter), ammonia is next added to precipitate the iron, the latter filtered off, washed, redissolved in nitric acid, and again precipitated by ammonia, filtered off, and washed. The filtrate is added to the one previously obtained, and the iron estimated in the precipitate and the copper in the united filtrates.

Assay of Copper Pyrites.

The following method of treating copper pyrites has been found more advantageous than the ordinary process of oxidising the mineral with aqua regia, and subsequently evaporating the solution repeatedly with hydrochloric acid, or with sulphuric acid, to expel the last traces of nitric acid. It is thus described by Mr. F. P. Pearson in the *Chemical News*:—

Place a weighed quantity of the powdered mineral, together with some potassium chlorate, in a porcelain dish. (Five grammes of a variety of a pyrites containing about 18 per cent. of copper was found to be enough for one analysis; and a quantity of potassium chlorate equal to a small teaspoonful was added to the ore.) Invert a small glass funnel with bent stem in the dish above the pyrites, and pour upon the latter rather more ordinary strong nitric acid than would be sufficient to completely cover the powder. Place the dish upon a water-bath, and, from time to time, throw into it small quantities of potassium chlorate. The doses of the chlorate must be repeated at frequent intervals, until free sulphur can no longer be seen in the dish. If necessary, add nitric acid, also, from time to time, to replace that lost by evaporation.

As a general rule, it is safer and more convenient to heat the mixture on a water-bath than upon sand, though the oxidation of sulphur can be effected more easily and quickly when the mixture of nitric acid and chlorate is heated to actual boiling than at the temperature obtainable by means of a water-bath. When the last particles of sulphur

have been destroyed, remove the inverted funnel from the dish, rinse it with water, and collect the rinsings in a beaker by themselves. Allow the liquid in the evaporating-dish to become cold, pour upon it a quantity of ordinary strong hydrochloric acid rather larger than the quantity of nitric acid taken at first, evaporate the mixed solution to dryness, and heat the dry residue to render the silica insoluble, in case any silica be present.

Pour water upon the cold residue, and, without filtering the liquor, wash the contents of the dish into the beaker which contains the rinsings of the funnel. Heat the liquid in the beaker nearly to boiling, add to it about 25 c.c. of a strong aqueous solution of ferrous sulphate slightly acidulated with sulphuric acid, and keep the mixture at a temperature near boiling during 4 or 5 minutes, in order to destroy the small quantity of nitric acid which may have escaped decomposition in spite of the evaporation with hydrochloric acid.

The ferrous salt seldom or never acts instantaneously, but the reducing action proceeds rapidly and perfectly satisfactorily when once begun. If need be, add more of the ferrous solution, little by little, until the entire contents of the beaker become dark-coloured or almost black, and no more gas is disengaged.

In order to be sure that all the nitric acid has been reduced, it is as well, after the mixture of liquid and solution of ferrous sulphate has been duly heated, to place a drop of the mixture upon porcelain, and test it with potassium ferricyanide. In general, however, the colouration of the liquor in the beaker, due to the formation of nitrous or hyponitric acid, will be a sufficient indication that the iron sulphate has done its work. The nitrous fumes quickly disappear from the liquid at a subsequent stage of operations when metallic iron is immersed in the solution.

When enough of the ferrous sulphate has been added, filter the mixed solution into a wide beaker, precipitate the copper in the metallic state upon a sheet of iron in the usual way, and ignite the copper in a porcelain crucible, in a current of hydrogen, before weighing it.

By means of the ferrous salt, the last traces of nitric acid may be got rid of far more quickly, conveniently, and certainly than by the old system of evaporating the pyrites solution with several successive portions of hydrochloric acid. By treating the pyrites with potassium chlorate and nitric acid, it is easy to oxidise and dissolve every particle of the sulphur in the mineral, so that no portion of the latter can escape decomposition by becoming enveloped in free sulphur. When aqua regia is used, on the other hand, or a mixture of potassium chlorate and hydrochloric acid, a certain proportion of sulphur almost invariably remains undissolved, and might easily enclose portions of the mineral, so as to protect them from the solvent action of the acids.

In determining copper in 'ore reducer' slags, Mr. T. C. Oland finds

that digestion with acid is not sufficient. A thorough disintegration of the slag is obtained by fusion with 4 parts of mixed potassium and sodium carbonates and $\frac{1}{2}$ part potassium nitrate. The fused mass is treated with dilute sulphuric acid, the liquid evaporated down to a convenient quantity, and the copper estimated electrolytically.

The Mansfeld Processes for Estimating Copper in Ores.

In that portion of Central Germany known as the Mansfeld District, there is found a vein containing metallic ore, which is worked for copper and silver. Generally speaking, however, this ore is extremely variable in value, and since it becomes more and more a matter of immense importance to be able to judge without loss of time of the quantity of metal contained in the ore brought up from various portions of the mines, the want of good means for ascertaining this speedily has long been felt. It need hardly be said that there exist a great many methods for the quantitative estimation of copper in its various combinations; but it is equally true that only very few of these are fit for technical application; and it is, moreover, especially desirable that persons not professional assayers or chemists, but superintendents of ordinary intelligence, should be enabled to make the required assays. In the laboratory of the mine-owners at Eisleben there has been in use for the poorer copper ores a method of assaying introduced by the late H. Rose, while the raw products of the furnaces were assayed according to a Swedish method. The objection against both these methods, which were executed by properly educated men, was, that for a large number of assays, such as are daily required to be finished there, it took too much time, too much room, and too many hands and apparatus. Rose's method just alluded to is the following:—The finely powdered ore is acted on by aqua regia, to which some sulphuric acid is added; next follow evaporation to dryness, dissolving in acidulated water, separation of the copper by means of sulphuretted hydrogen, and weighing the copper sulphide after having been ignited and cooled in a current of hydrogen gas. Although the method here described is a good one, it involves for correctness the condition that no metals precipitable by sulphuretted hydrogen, and non-volatile when ignited in a current of hydrogen, be present. As regards the Mansfeld ores, the absence of such metals has been repeatedly proved; but for all this, it appears that now and then small quantities of molybdenum have affected the correctness of the results.

The Swedish method, however excellent its results, is very cumbersome, and embraces too many different operations to admit of being very readily and thoroughly mastered by many operators. The chief difficulty as regards it is the precipitation of the metallic copper by means of metallic iron; the solution from which it takes place should neither be too hot nor too cold; a large excess of acid also is objectionable. It requires, moreover, a special tact to see when all the

copper has been precipitated, since the iron must then be removed from the solution at once, and the acid solution decanted from the copper; in one word, with the greatest possible care, it was not very easy to work the two methods just briefly alluded to with operators who were not specially educated for such work.

Under these circumstances, the directors of the Mansfeld copper mines issued, in May 1867, an advertisement offering a prize of 45*l.* to anyone who would discover a method of assaying the Mansfeld copper ores which would fulfil certain specified conditions.

To this advertisement 16 answers were received. Six of the proposed methods were based on the volumetric estimation of copper by means of potassium cyanide or sodium sulphide. One proposed method was based upon the estimation of iodine previously set free by means of sodium thiosulphate; one was by titration with solution of iodine; one by titration with potassium permanganate; one by titration with potassium sulphocyanide; one by estimation of copper as oxide; two by estimations of copper as sulphide, combined with ignition in current of hydrogen gas; two by a so-called process of dry assay; one by a process by electrolysis.

In order to select from this material, and report upon the best and most suitable plan, a committee of three gentlemen was appointed; two of them practical assayers and copper-smelters, the third the well-known Dr. Böttger. This committee decided:—

(a). That any process which included many operations, and consequently took up too much time, is to be excluded.

(b). No process is to be admissible which involves the use of varying quantities of ore, since it is impossible to judge by sight of the quality of the Mansfeld ore.

(c). Any process is also inadmissible wherein, for the burning off of the bituminous organic matter of the ore, expensive substances, as, for instance, potassium chlorate, are recommended.

(d). Any process is likewise inadmissible wherein the reactions take place with great violence, and may thus induce explosions.

(e). Those methods are also inadmissible wherein, for quantities of 5 grammes and more, the treatment with acids and evaporation to dryness after addition of sulphuric acid are necessary.

(f). On sanitary grounds, and in reference to the large number of operations and assays daily required, such processes are also inadmissible wherein sodium thiosulphate is employed so that sulphurous acid is given off; while processes wherein large bulks of sulphuretted hydrogen are used are equally discarded.

(g). Methods whereby copper is separated from the earths, iron oxides and other metallic oxides, either by ammonia alone, or by ammonium carbonate, tartaric acid, &c., in addition thereto, are also discarded; because the precipitated iron oxide or alumina never fails to carry down some copper also; and, also, because oxides like

those of zinc, nickel, and cobalt, by remaining in solution, affect the accuracy of the estimation of copper.

(h). Those estimations of copper are also discarded whereby it is collected in a spongy state, or as sulphide upon previously dried and weighed filters.

(i). The dry assay is also discarded, as, even if it were possible to obtain therewith correct results, it would entail too great expenditure in the consumption of fuel, breaking up of apparatus, crucibles, &c., and the use of various fluxes.

(k). Those processes are also discarded which require in the operator too much scientific training.

(l). Those which require the aid of assistants are also discarded.

It is clear that many persons who had entered into the competition on this subject could not, owing to the severe conditions, remain in the field. The umpires instituted a large number of assays with divers samples of ores, which had been previously analysed, and the composition of which had been estimated with rigorous accuracy, but had not been communicated to them. Their researches proved that, as regards the methods of volumetric estimation, only such deserve any confidence where the copper has been first previously separated in a metallic state, and next redissolved; and that then only the titration method with potassium cyanide is trustworthy.

After a long series of experiments, the umpires decided in favour of Dr. Steinbeck's method in the first place, but were at the same time so satisfied respecting M. C. Luckow's plan, that to that gentleman, who holds the position of chief chemist to the Cologne-Minden Railway Company at Deutz, a premium was also awarded. These two processes are given in the following pages.

Estimation of Copper in the Mansfeld Ores by Dr. Steinbeck's Process.

This method, which entirely answers the imposed conditions, embraces three distinct operations, viz.:—1. The extraction of the copper from the ores. 2. The separation. 3. The quantitative estimation of that metal.

1. The Extraction of the Copper from the Ore.—A proof centner, equal to 5 grammes of pulverised ore, is put into a flask, and there is poured over it a quantity of from 40 to 50 c.c. of crude hydrochloric acid, of a sp. gr. of 1.16, whereby all carbonates are converted into chlorides, while carbonic acid is expelled. After awhile, there is added to the fluid in the flask 6 c.c. of a normal nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1.2 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld, some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead

of 6. The flask containing the assay is digested on a well-arranged sand-bath for half an hour, and the contents only boiled for about 15 minutes, after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or at the most only 0.01 to 0.08 per cent. has been left undissolved.

The extraction of the copper from the ore, according to this method, is complete, even in the case of the best quality of ore, which contains about 14 per cent. of metal; while, at the same time, the very essential condition for the proper and complete separation of the metal, viz. the entire absence of nitric acid or any of the lower oxides of nitrogen, is fully complied with.

2. Separation of the Copper.—The solution of metallic and earthy chlorides, and some free hydrochloric acid, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker of about 400 c.c. capacity: in this beaker has been previously placed a rod of metallic zinc, weighing about 50 grammes, and fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as much as possible free from lead, and at any rate not contain more than from 0.1 to 0.3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in already during the filtration of the warm and concentrated fluid, and is, owing chiefly to the complete absence of nitric acid, completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the fluid be tested with sulphuretted hydrogen, no trace even of copper will be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and, in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must be always employed) has been removed, the spongy metal is repeatedly and carefully washed by decantation with fresh water, which need not be distilled, and care is taken to collect together every particle of the spongy mass.

3. Quantitative Estimation of the Precipitated Copper.—To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the normal nitric acid are added, and the copper is dissolved by the aid of moderate heat, as copper nitrate; in the event of any small quantity of lead being present, it will of course be contaminated with lead nitrate.

When copper ores are dealt with which contain above 6 per cent. of copper, which may be sufficiently judged from the larger bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are employed for dissolving the spongy metallic mass. The solution thus obtained is left to cool, and next, immediately before titration

with potassium cyanide, mixed with 10 c.c. of normal solution of ammonia, prepared by diluting 1 volume of liquid ammonia, sp. gr. 0.98, with 2 volumes of distilled water.

In the case of ores which yield over 6 per cent. of copper, and where a double quantity of normal nitric acid has consequently been used, the solution of copper in nitric acid is diluted with water and made to occupy a bulk of 100 c.c.; this bulk is then divided exactly into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of the liquid ammonia solution just alluded to, and the copper therein volumetrically determined. The deep blue-coloured solution of copper oxide in ammonia only contains besides, ammonium nitrate, any lead which might have been dissolved having been precipitated as hydrated lead oxide, which does not interfere with the titration with potassium cyanide. The solution of the last-named salt is so arranged that 1 c.c. thereof exactly indicates 0.005 gramme of copper. Since, for every assay, 5 grammes of ore have been taken, 1 c.c. of the titration fluid is, according to the following proportion,— $5 : 0.005 :: 100 : 0.1$,—equal to 0.1 per cent. of copper; it hence follows that, by multiplying by 0.1 the number of the c.c. of potassium cyanide solution used to make the blue colour of the copper solution disappear, the percentage of copper contained in the ore is immediately indicated.

As may be imagined, at the laboratory of the mine-owners at Eisleben, such a large number of assays are daily executed that, in this case, there can be no reason to fear a deterioration of the cyanide solution, of which large quantities are used and often fresh made; but for security's sake, the solutions are purposely tested for control at least once every week. According to the described plan, 6 assays can be made within 4 hours; and during a working day of from $7\frac{1}{2}$ to 8 hours, 20 assays have been often quite satisfactorily made by the umpires, as well as by the workmen at Eisleben.

Special Observations on this Method.—Dr. Steinbeck considered it necessary to test his method specially, in order to see what influence is exercised thereupon by (1) ammonium nitrate, (2) caustic ammonia, (3) presence of lead oxide. The copper used to perform the experiments for this purpose was pure metal, obtained by galvanoplastic action, and was ignited to destroy any organic matter which might accidentally adhere to it, and, next, cleaned by placing it in dilute nitric acid. Five grammes of this metal were placed in a litre flask and dissolved in 266.6 c.c. of normal nitric acid, the flask and contents gently heated, and, after cooling, the contents diluted with water, and thus brought to a bulk of 1000 c.c. exactly. Thirty c.c. of this solution were always applied to test and titrate one and the same solution of potassium cyanide under all circumstances. When 5 grammes of ore, containing on an average 8 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0.15 gramme

of the chemically pure copper. The quantity of normal nitric acid taken to dissolve 5 grammes of pure copper (266·6 c.c.) was purposely so taken as to correspond with the quantity of 8 c.c. of normal nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is exactly met with in 80 c.c. of the solution of pure copper.

As regards No. 1 and No. 2 (see above), the influence of double quantities of ammonium nitrate and free caustic ammonia (the quantity of copper remaining the same), and the action of dilute solution of potassium cyanide thereupon, will become elucidated by the following facts:—

(a). Thirty c.c. of the normal solution of copper, containing exactly 0·15 gramme of copper, were rendered alkaline with 10 c.c. of normal ammonia, and are found to require, for entire decolouration, 29·8 c.c. of potassium cyanide solution; a second experiment, again with 80 c.c. of normal copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide solution. The average of the two experiments is 29·85 c.c.

(b). When to 80 c.c. of the normal copper solution first 8 c.c. of normal nitric acid are added, and then 20 c.c. of normal ammonia solution, instead of only 8, whereby the quantity of free ammonia and of ammonium nitrate is made double what it was in the case of the experiments spoken of under (a), there is required of the same cyanide solution 80·8 c.c. to produce decolouration. A repetition of the experiment, under exactly the same conditions, gave 80·4 c.c. of the cyanide solution employed; the average of both experiments is, therefore, 80·85 c.c.

The difference between 80·85 and 29·85 is equal to 0·5 c.c., and that figure is therefore the coefficient of the influence of double quantities; and supposing this to happen with the ores in question, it would only be equivalent to 0·05 per cent. of metallic copper. It is hence clear that slight aberrations of from 0·1 to 0·5 c.c. in the measuring out of 8 c.c. of normal nitric acid, used to dissolve the spongy copper, and of 10 c.c. of normal ammonia, in order to render that nitric acid copper solution alkaline, is of no consequence whatever for the technical results to be deduced from the assay; it should, moreover, be borne in mind that the quantities of free ammonia and of ammonium nitrate in the actual assay of ores, for which always a quantity of 5 grammes of ore is taken, vary according to the richness or poverty of the ores in copper; and the quotations of the following results of experiments prove that the influence of these substances is only very slightly felt in the accuracy of the results:—

Eight c.c. of the normal nitric acid have been found to contain, by means of a series of experiments, 1·358 gramme of anhydrous nitric acid; and this quantity of acid is exactly neutralised by 7·7 c.c. of normal ammonia solution, which contains 0·6515 gramme of ammonium

oxide ; and 10 c.c. of the said normal solution contain 0.846 gramme of ammonium oxide.

One gramme of metallic copper requires, for complete oxidation, 0.2523 gramme of oxygen, and this quantity of oxygen is given off by 0.5676 gramme of anhydrous nitric acid ; while, at the same time, nitrogen binoxide is disengaged. From these data can be calculated (1) the quantity of nitric acid which becomes decomposed when variable quantities of metallic copper are dissolved therein ; (2) what quantity of nitric acid is left to form neutral ammonium nitrate ; and (3) what quantity of free ammonia will be left after a portion of that alkali has been combined with, and therefore neutralised by, copper oxide ; and any remaining free nitric acid.

It is found that the quantitative variations between ores containing 1 per cent. or 6 per cent. of metal vary very little from the normal quantities exhibited by ores containing 8 per cent. of metal. The relation is as 1 : 2 ; and, for technical purposes, this has been proved not to be a disturbing quantity.

When, however, larger quantities of ammoniacal salts are present in the fluid to be assayed for copper, by means of a titrated solution of potassium cyanide, and especially when ammonium carbonate, sulphate, and, worse still, chloride, are simultaneously present, these salts exert a very disturbing influence.

The presence of lead oxide in the copper solution to be assayed has the effect of producing, on the addition of ammonia, 10 c.c. of normal ammonia, a milkiness along with the blue tint ; but the presence of this oxide does not at all interfere with the estimation of the copper by means of the cyanide, provided the lead be not in great excess ; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Dr. Steinbeck, however, purposely made some experiments to test this point, and his results show that neither 50 nor 100 per cent. of addition of lead exerts any perceptible influence upon the estimation of copper from its ores, or otherwise, by means of potassium cyanide. A small quantity of lead accidentally occurring will not, therefore, affect the results, and this the less so as, generally, no ores of both metals occur together wherein both are met in sufficient quantity to make it worth while working the ore for both metals at the same time.

Since it is well known that the presence of zinc very perceptibly influences the action of a solution of potassium cyanide, when applied to the volumetrical estimation of copper, Dr. Steinbeck considered it necessary to institute some experiments, in order precisely to ascertain with what quantity of zinc present along with copper this influence commences to become perceptible. The solution of zinc employed was made by dissolving the metal in the smallest possible quantity of nitric acid ; and 1 c.c. of that solution contained 0.001 gramme of zinc. The results of the experiments show that the presence of zinc does not

interfere with the visibility of the end of the reaction, viz. the decolouration of the copper solution. They also prove that a small quantity of zinc, less than 5 per cent. of the quantity of copper present, or 0.0075 gramme by weight of zinc, does not at all affect the action of the solution of potassium cyanide, but when the quantity of zinc increases, a very perceptible effect is seen upon the solution of cyanide; it is therefore necessary to bestow due care while washing the spongy copper, after it has been precipitated by means of zinc from its solution.

Since it has been ascertained that the action of solution of potassium cyanide in researches of this kind is also affected by an increased temperature of the solution of copper which is to be titrated therewith, it is strictly necessary never to operate with warm ammoniacal solutions of copper, but to suffer the same to cool down to the ordinary temperature of the air of the laboratory.

While 80 c.c. of copper solution, containing 0.15 gramme of copper and 10 c.c. of normal ammonia solution, required, at the ordinary temperature, 80 c.c. of cyanide solution; the same quantities required, at between 40° to 45° C., 28.8 c.c. of solution of cyanide; and at 45° C., 28.9 c.c. of the same solution, thus proving the injurious effect of warm solutions.

Estimation of Copper in the Mansfeld Ores by M. C. Luckow's Process.

This gentleman has applied to the quantitative estimation of copper a new method, based upon the precipitation of the metal in the metallic state from solutions containing either free sulphuric or nitric acids, by means of a galvanic current.

It is a great advantage of this method, that, while the copper is precipitated, it is simultaneously separated from metals with which it is often found alloyed; some of these, such as tin and antimony, are separated by treatment with nitric acid in an insoluble form, while others, like silver, can easily be removed in the form of chloride. It is, at the same time, another advantage that the state in which the copper is obtained admits of its being accurately weighed and estimated, while a great number of operations, which require much time and various apparatus, are at the same time got rid of.

Although M. Luckow had previously discovered a method of electro-metallic analysis from fluids containing free sulphuric acid, his researches on the same subject, in the case of free nitric acid, belong to a recent period. These researches brought very unexpectedly to light the curious fact that even a weak galvanic current had the power of completely precipitating copper in a pure metallic state from nitric solutions, provided they did not contain more than 0.1 gramme of anhydrous nitric acid to the c.c. (nitric acid of 1.2 sp. gr. contains 0.82 gramme of anhydrous nitric acid to the c.c.), while it was found that

the action was, at the same time, more regular, and less dependent upon the power of the current than when free sulphuric acid was present. The following more commonly occurring metals are *not* precipitated by galvanic action from acid solutions:—Zinc, iron, nickel, cobalt, chromium, the metals of the earths, and alkalis. The following are precipitated (*a*) in the shape of peroxides, at the positive electrode completely, lead and manganese; incompletely, silver. When the solution contains traces of manganese, it becomes, in consequence of the formation of a trace of manganese peroxide, or of permanganic acid, deeply violet-coloured. This very sensitive reaction for manganese also takes place when small quantities of chlorine are present. The presence in the fluid of oxalic, lactic, and tartaric acids, and other readily oxidisable organic substances, and such protoxides as are readily peroxidised—for instance, iron protoxide—retard the formation of peroxides, as well as the occurrence of the reaction of manganese.

(*b*) Mercury, silver, copper, and bismuth are precipitated at the negative electrode in the metallic state. When mercury is present in the solution simultaneously with copper, the former metal is separated before the latter, in the fluid metallic state. As soon, however, as the precipitation of copper commences, an amalgam of the two metals is formed when mercury is also present. Silver is precipitated almost simultaneously with copper; bismuth only begins to be precipitated after the greater portion of the copper has been separated. A complete separation of silver only ensues when some such substance as tartaric or other similar acid is simultaneously present in the solution. The separation of the three last-named metals, by means of galvanic action, is, therefore, unsuccessful; but, fortunately, there are many other means to accomplish this end completely.

(*c*) Metallic arsenic is only precipitated slowly, and long after the complete separation of copper, if arsenic acid happen to be present. The same remark applies to antimony, since it is well known that small quantities of antimonious acid are soluble in nitric acid.

The operations, according to Luckow's plan, are—1. Roasting the ore. 2. Solution of the roasted product. 3. Precipitation of the copper. 4. Weighing the copper.

1. Roasting the Ore.—Care should be taken to obtain a finely-ground average sample of the ore. Then weigh off, in small porcelain capsules previously counterpoised, quantities of from 1 to 3 grammes; these quantities are then placed on the inverted lid of an iron crucible, on the inner surface of which the powdered ore is heated over the flame of a Bunsen gas-burner. The powder may be carefully stirred up with a platinum wire, to promote the access of air during the roasting; the ignition of bituminous matter and sulphur will be ended in about 7 minutes. Ores which do not contain bitumen at all need not be roasted.

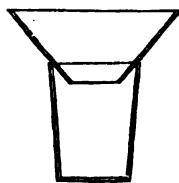
It has been already stated that in the case of poor copper ores (and

those of the Mansfeld district are generally so), the quantities to be weighed off for assay should not vary according to a presumed percentage of copper. Two grammes are therefore taken, and, instead of roasting the ore on the lid of an iron crucible, small porcelain crucibles are applied for that purpose.

2. Solution of the Roasted Product.—The iron lid is suffered to cool, the roasted powder placed on a piece of glazed paper, and any powder adhering to the lid is removed by means of a camel's-hair brush on to the paper. The powder is next transferred to small beaker glasses, and about 2 or 3 c.c. of nitric acid, of 1.2 sp. gr., are added, along with about 10 to 15 drops of concentrated sulphuric acid. The beakers are then placed on a sand-bath, and moderately heated, at first; but when the contents have nearly become dry, the heat is increased, so as to evaporate and expel all sulphuric acid. The beakers should be covered with perforated watch-glasses. This operation requires from about three-quarters of an hour to one hour. The addition of sulphuric acid is made in order to increase the oxidising action of the nitric acid, and also to convert any lime which may happen to be present in the ore into a difficultly soluble salt. It is very useful, also, to add from 10 to 20 drops of hydrochloric acid to the mixture of the two acids just alluded to, since the rapidity of the evaporation is thereby increased and the occasional spirting about of the fluid is lessened.

The process just described may be modified, first by the use of porcelain capsules, the contents of which are easily transferred to beakers with flat bottoms, not higher than about 2 inches altogether. It is better, also, to use a sulphuric acid, prepared with equal bulks of concentrated acid and water, and to measure off 4 c.c. for each assay; while for each assay, moreover, 6 c.c. of nitric acid and about 25 drops of hydrochloric acid are taken. Instead of covering the beaker with a perforated watch-glass, the upper part of a funnel is used, as represented in Fig. 4; with this arrangement the sulphuric acid evaporates far more readily, and loss by spirting is prevented. The beaker is heated on a well-arranged sand-bath.

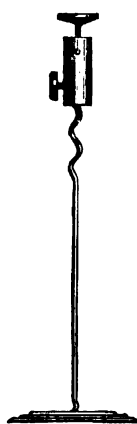
FIG. 4.



8. Precipitation of the Copper.—As soon as the beaker after removal from the sand-bath has become quite cool, the funnel which has been used as a cover is washed on both sides, inner and outer, with nitric acid of 1.2 sp. gr., diluted with 6 times its bulk of pure water; the sides of the beaker are next likewise washed, and it is then filled to about half its height with the same acid. A few drops of a concentrated solution of tartaric acid are added (this acid is best kept in solution in open vessels, only slightly covered with a piece of paper); this having been done, the wire spiral, represented in Fig. 5, is carefully placed in the beaker. This spiral consists of a piece of

platinum wire, about $\frac{1}{8}$ of an inch thick and $7\frac{1}{2}$ inches long, $\frac{2}{3}$ of its length being so wound that the straight end of the wire projects

FIG. 5.



as if it were the axis of the centre of the spiral. The convolutions of the spiral are so large that they touch the sides of the beaker, while the straight portion just touches the centre of the bottom of the vessel.

When the heating has been carefully attended to, the acid fluid added to the contents of the beaker, after evaporation to dryness, will generally be quite clear; if it happens to be turbid, 1 or 2 c.c. of a concentrated solution of barium nitrate may be added, and the thorough mixing of this saline solution with the acid contents of the beaker promoted, by gently moving up and down the platinum spiral just alluded to, and allowing the fluid to rest for a few minutes after. The copper present in the mass left at the bottom of the beaker gradually dissolves, and it is not actually requisite to wait before applying the galvanic current until it is all dissolved.

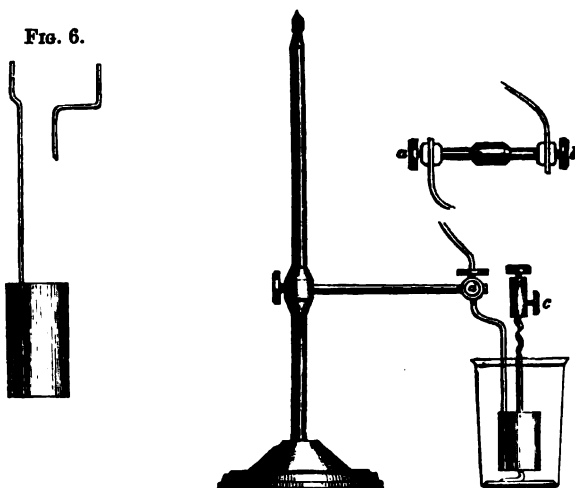
The next point is to place in the beaker the platinum foil, represented at Fig. 6, of which the dimensions are—length, $2\frac{1}{2}$ inches; width, $1\frac{1}{4}$ inch. The lower end of this platinum foil should be kept about $\frac{1}{8}$ of an inch apart from the convolutions of the spiral. When the beaker is only half filled with liquid, the platinum foil is immersed in the same for more than $\frac{3}{4}$ of its height. The wire fastened to this foil is fixed, by means of a screw, *a*, to the arm, *a b*, of the stand, represented at Fig. 7; the other screw, *b*, serves to fasten a copper wire, proceeding from the zinc end of the galvanic battery. When the small screw clamp, *c* (Fig. 7), has been fastened to the platinum wire placed in the beaker, another wire is fastened in the top opening of the clamp, and this wire connected with the copper end of the battery, and the galvanic circuit thus closed. In a few moments after this has been done, the platinum foil, bent in the shape of the cylinder and placed inside the beaker, as before described, will be observed to become covered with a coating of metallic copper, while from the platinum spiral wire bubbles of gas escape, which facilitate, to some extent, the solution of the copper oxide in the dilute acid.

In order to ascertain whether the whole quantity of the copper has been precipitated, some more dilute nitric acid is added to the fluid in the beaker. If, in 10 minutes after this, no more metallic copper is separated on the clean portions of the platinum foil, the operation is finished.

It must be here observed that continued practice has proved that the addition of a concentrated solution of barium nitrate acts injuriously on the process, as the metallic copper, which becomes separated, gets mixed with some insoluble barium sulphate, which increases the weight of the substance to be weighed.

The time occupied by the complete precipitation of the metal varies according to the force of the galvanic current. It takes from 3 to even 8 hours. In order to make this point certain, all test assays are left for 8 hours consecutively to the action of the galvanic current, experience having proved that, after that lapse of time, even with a weak current, the precipitation was so complete that all chemical reagents for detecting the presence of copper failed to discover the most minute trace of that metal.

FIG. 7.



4. Weighing the Copper.—The platinum cylinder to which the copper adheres, and the platinum wire spiral, are disconnected from the galvanic apparatus, the platinum cylinder carefully removed from the beaker and immediately plunged into a beaker filled with fresh cold water, and rinsed therein; next washed with alcohol, by means of a washing-bottle, and then dried in a drying apparatus, and weighed after cooling. Since the platinum cylinder has been very accurately weighed *before* the experiment, its increase in weight will, of course, be that of the copper obtained.

The process here described has been somewhat modified and greatly improved upon at Eisleben, where it is in constant use, by the employment of a series of galvanic elements. It is, in the first place, found better not to disconnect the galvanic current while the copper is yet in contact with acid, so that, instead thereof, the acid fluid in the beaker is replaced by turning in a stream of water, and suffering the same to run over the sides of the beaker, and to be received into a proper vessel to hold it. In this manner all the acid is displaced, without risk of any very small quantity of copper becoming acted upon by the acid during the brief period elapsing between the disconnecting

of the galvanic current and the removal from the beaker of the platinum cylinder and spiral wire. These parts, on being removed, are carefully washed, first with boiling water, next with alcohol, and then dried at a temperature of about the boiling-point of water. The cylinder is then weighed, the copper coating is removed by means of nitric acid; the platinum is next washed in water, dried, and again weighed.

There are in use at Eisleben 9 galvanic batteries (lead and zinc elements); these yield 18 assays ready for weighing in 24 hours; and it would not be difficult for the persons there employed to work with 12 batteries each of 3 elements. The results obtained are highly satisfactory. The following observations may be made in reference to this method:—

(a). The quantity of ore taken for trial is 2 grammes; this is found sufficient, while it consumes less acid.

(b). The evaporation of the acid is carried on to complete dryness on the sand-bath. Spiriting of the fluid is easily prevented.

When the copper has been precipitated properly it will show its peculiar colour on the surface, and the good success of the operation may also be judged from the fact that no saline matter adheres to the platinum; the complete absence of this saline matter has been found to be evidence of perfect removal of the copper from the fluid.

The process just described is especially applicable for rather poor ores, such as do not contain above 7 or 8 per cent. of copper. Each assay, from beginning to end, takes 10 hours for complete analysis; but it is evident that the greater portion of this period does not give active employment to the assayer. The expense of working this process, after the apparatus has been once purchased, is very small. The process may also be applied to analyse richer ores, and also alloys of copper, with some slight modifications which will readily suggest themselves.

Mr. J. B. Mackintosh, of Hoboken, New Jersey, states that he had made a series of experiments with the Luckow electrolytic estimation of copper. Mr. Mackintosh describes the manner in which he adapted the Luckow method to the analysis of copper alloys as follows:—He dissolves the alloy in nitric acid, evaporates the solution to dryness to get rid of the excess of acid, dissolves the residue in water with the addition of a few drops of nitric acid to dissolve the basic copper nitrate formed, and to this solution adds 4 or 5 drops of a concentrated solution of citric acid. This solution is then precipitated in a platinum dish with a current from 2 Bunsen cells of about 1 quart capacity. In precipitating several samples at once it is arranged so that the whole current traverses the row of dishes, the negative pole of each set being connected with the positive pole of the next succeeding one. In this case, if n be the number of dishes, then $n+1$ is the number of battery-cells of that size used.

Mr. Mackintosh has followed up the matter, analysing the copper deposited, in which he estimated carbon, hydrogen, and nitrogen; and he comes to the conclusion that some organic matters, and in all probability all, in the presence of nitric acid in the copper solution undergoing electrolysis, cause erroneous results; that from a nitric acid solution, with no organic matter, it is extremely difficult to separate all the copper; and that the old method of electrolysis from the sulphate is the best.

Mr. C. Luckow has taken up the matter in the *Chemiker Zeitung*, in which he states that he added tartaric acid to the nitric solution of copper only with the special purpose of preventing the injurious action of manganese salts when present, with special reference to the assay of the Mansfeld copper shales. He states also that the form of the apparatus was designed with that object in view. He advises that tartaric acid be dispensed with, except when small quantities of manganese are present, and says it is easy to deposit the copper from the solution holding free nitric acid; it can be taken to drive off nitrous acid, and not to use too strong a current.

Detection of Minute Traces of Copper in Iron Pyrites and other Bodies.

Although an exceedingly small percentage of copper may be detected in blowpipe experiments by the reducing process, as well as by the azure-blue colouration of the flame when the test-matter is moistened with hydrochloric acid, these methods fail in certain extreme cases to give satisfactory results. It often happens that veins of iron pyrites lead at greater depths to copper pyrites. In this case, the iron pyrites will almost invariably hold minute traces of copper. Hence the desirability, on exploring expeditions more especially, of some ready test by which, without the necessity of employing acids or other bulky and difficultly portable reagents, these traces of copper may be detected. The following simple method is due to Dr. E. Chapman, Professor of Mineralogy and Geology, Toronto, and will be found to answer the purpose:—The test-substance, in powder, must first be roasted on charcoal, or, better, on a fragment of porcelain¹ in order to drive off the sulphur. A small portion of the roasted ore is then fused on platinum wire with phosphor salt, and some potassium bisulphate

¹ In the roasting of metallic sulphides, &c., small fragments of Berlin or Meissen porcelain, such as result from the breakage of crucibles and other vessels of that material, may conveniently be used. The test-substance is crushed to powder, moistened slightly, and spread over the surface of the porcelain; and when the operation is finished, the powder is easily scraped off by the point of a knife-blade or small steel spatula. In roasting operations, rarely more than a dull-red heat is required; but these porcelain fragments may be rendered white-hot, if such be necessary, without risk of fracture.

is to be added to the glass (without this being removed from the wire) in 2 or 3 successive portions, or until the glass becomes more or less saturated. This effected, the bead is to be shaken off the platinum loop into a small capsule and treated with boiling water, by which either the whole or the greater part will be dissolved; and the solution is finally to be tested with a small fragment of potassium ferrocyanide. If copper be present in more than traces, this reagent, it is well known, will produce a deep red precipitate. If the copper be present in smaller quantity—that is, in exceedingly minute traces—the precipitate will be brown or brownish-black; and if copper be entirely absent, the precipitate will be blue or green—assuming, of course, that iron pyrites or some other ferruginous substance is operated upon. In this experiment the preliminary fusion with phosphor salt greatly facilitates the after solution of the substance in potassium bisulphate. In some instances, indeed, no solution takes place if this preliminary treatment with phosphor salt be omitted.

Another very delicate method of detecting traces of copper before the blowpipe by the employment of silver chloride will be found in a subsequent chapter.

Estimation of Copper Suboxide in Metallic Copper.

When dilute sulphuric acid acts upon copper suboxide in the presence of silver nitrate, the suboxide is split up into metallic copper and copper oxide, the latter becomes dissolved as sulphate, while the metallic copper takes the place of the silver of the nitrate of that metal. In order to apply this reaction for analytical purposes, M. C. Aubel takes 0.5 gramme of the copper to be tested, previously reduced, by proper mechanical means, to powder or filings; and adds to it 1.3 gramme of solid silver nitrate mixed in a mortar with 10 c.c. of dilute sulphuric acid. The decomposition sets in at once, and is entirely complete after 2 hours' time; water is then added, the metallic silver is collected on a filter, well washed, and, after having been dried, is weighed. From its weight the amount of suboxide which was present is easily calculated.

Separation of Copper and Uranium.

Sergius Kern proposes to precipitate the mixed solution of the two metals, very feebly acid, with potassium ferrocyanide and treat the mixed precipitate with dilute hydrochloric acid. The uranium ferrocyanide dissolves whilst the corresponding copper compound remains undissolved.

Uranium ferrocyanide dissolved in hydrochloric acid, and boiled with a few drops of nitric acid, gives a green colouration. This reaction is proposed as a test for uranium salts.

Separation of Copper from Mercury.

Copper and mercury are conveniently separated by the addition of phosphorous acid to the dilute hydrochloric solution of the two metals. On standing for some time in the cold, the mercury is precipitated in the form of protochloride. The filtrate is heated to ebullition, and the copper oxide precipitated by caustic potash.

Separation of Copper from Silver.

The ordinary methods of separating copper from silver are too simple to require mention here. It may happen, however, that a rapid and approximate separation of silver and copper nitrates is wanted without resorting to the process of precipitating the silver as metal or as chloride. Under these circumstances the following process will be useful. (It is supposed that the object is to prepare silver nitrate from silver coins which contain a large percentage of copper.) The alloy is dissolved in nitric acid; the solution is filtered if necessary, and evaporated until it has the consistency of a thickish oil; when this point is reached there is added to the solution very concentrated nitric acid free from hydrochloric acid. By this proceeding all the silver nitrate is precipitated, while copper nitrate remains in solution. One part of the concentrated metallic solution requires from 8 to 4 parts of nitric acid for the complete precipitation of the silver nitrate; the more concentrated the nitric acid is the better, but acid of 1.25 sp. gr. answers the purpose. The solution of copper is decanted off and the silver nitrate washed with nitric acid.

A more exact but somewhat more troublesome method is to fuse the mixed nitrates. Copper nitrate decomposes much more readily than silver nitrate.

Separation of Copper from Nickel or Cobalt.

Obtain the metals in a slightly acid solution, and add sulphurous acid till the copper is entirely reduced to the state of sub-salt. Then precipitate with potassium sulphocyanide, and after allowing the precipitate to digest in the liquid for a short time, filter off the white copper subsulphocyanide.

The ordinary process for separating copper from nickel, founded on the precipitation of copper by sulphuretted hydrogen, leaves much to be desired on account of the facility with which copper sulphide after washing passes to the state of sulphate; and also because copper, during precipitation, always carries down with it considerable quantities of nickel, which passes to the state of sulphide in the precipitate. M. Dewilde has worked out a method of separating these metals based upon the property possessed by glucose of precipitating copper as a sub-oxide, when that metal exists in the form of tartrate dissolved by the aid of caustic potash. His process is as follows:—

Dissolve about 2 grammes of the alloy in hydrochloric acid containing a little nitric acid; evaporate off the excess of acid and dissolve the mixed chlorides in about 50 grammes of water. To the solution add about 4 grammes of cream of tartar. Heat slightly to facilitate solution, and add gradually a solution of caustic potash in alcohol. The first addition of alkali precipitates the copper and nickel oxides in the state of hydrates, but an excess of potash redissolves the whole, the copper and nickel tartrates being soluble in caustic potash. A blue solution is thus obtained, which after cooling is treated by a solution of pure glucose or inverted sugar, and boiled for 1 or 2 minutes. The copper is precipitated as a beautiful red suboxide sinking quickly to the bottom of the vessel; if, however, the glucose is added to a warm solution, the copper is precipitated in flakes which it is difficult to wash. The completion of the precipitation is ascertained by adding a further quantity of the glucose solution.

The precipitated copper suboxide is washed, dried, and ignited. It may be heated with nitric acid, and copper protoxide obtained by igniting the nitrate so obtained.

The filtrate containing the nickel is evaporated to dryness, the residue calcined, and then washed to remove the potassium carbonate. As the incineration can never be complete, on account of the presence of this salt, the operation is to be repeated. The residue, consisting chiefly of nickel oxide, is dissolved in aqua regia, and the hydrated nickel oxide precipitated from the solution by caustic potash. It is very difficult, if not impossible, to wash this very voluminous oxide, so the best plan is to wash incompletely, dry, and slightly calcine the oxide; after grinding this in an agate mortar, it is easily freed from the last trace of potash by washing in warm water. The oxide thus obtained is reduced in a platinum crucible in an atmosphere of hydrogen.

This process is in use in the Belgian mint, where copper and nickel alloys are used for coinage.

Separation of Copper from Zinc.

The solution of copper and zinc must contain no other metal which forms an insoluble iodide. Add sulphurous acid to the solution, and then, after gentle heating, potassium iodide until the supernatant liquid has lost its blue colour and a precipitate is no longer formed. There should be a slight excess of sulphurous acid the whole time. The copper subiodide being very dense deposits readily, especially on warming, like silver chloride. Heat to the boiling-point and collect on a weighed filter. The precipitate, washed with warm water, is dried at 120° and weighed. All the zinc will be in the solution.

Another very perfect method of separating copper from zinc consists in dissolving in nitric acid, evaporating to dryness, and heating to redness, so as to leave a mixture of copper and zinc oxides. Finely powder

these oxides, and introduce them by means of a platinum boat into a small light glass tube, furnished with a good cork. The weight of the boat, tube, and cork being already known, another weighing, after having heated them to redness in a current of air, gives the weight of the mixture of oxides. The boat is then introduced into a combustion-tube, and a current of dry hydrogen is passed over, whilst heat is applied sufficient to reduce the copper oxide. When the boat and its contents cease to lose weight, remove them to the small corked tube, allow to cool, and weigh. The contents of the boat will now consist of zinc oxide and metallic copper, and from the amount of oxygen lost the quantity of copper present may be ascertained with accuracy. (Supposing no impurities are present, the loss, multiplied by 5, gives very nearly the amount of copper present, and if the object has been merely to ascertain the composition of a sample of brass, the operation may be terminated; otherwise, it may be concluded as follows.) Prepare dilute sulphuric acid, perfectly freed from nitroxygen compounds, by distillation over ammonium sulphate, heat the acid to completely free it from air, and pour it over the mixture of zinc and copper oxide in a small stoppered flask. The zinc oxide will be dissolved, whilst the metallic copper will remain intact. After allowing the mixture to rest for some hours, decant and wash the copper several times in boiled water. The solution contains all the zinc; evaporate to dryness, heat to about 400°C. , and weigh as anhydrous sulphate.

For the assay of cupriferous blende, R. Monger proceeds as follows: Half a gramme of the blende is treated with aqua regia and evaporated; it is re-moistened with hydrochloric acid and re-evaporated; dissolved in water with a drop or two of hydrochloric acid, 10 to 20 c.c. of ammonia are added, and the iron is filtered off and washed. The filtrate, which is now from 200 to 250 c.c. in volume, is acidified with hydrochloric acid, heated and placed in a porcelain dish. Sodium sulphide solution is added, enough to precipitate the whole of the copper and leave a little excess, and the liquid is then titrated with ferrocyanide at 0.01 strength, using uranium acetate as indicator.

Separation of Zinc from Metals of the Copper and Iron Group.

W. Alexandrowicz shows that the separation of zinc from these metals presents considerable difficulties. The quantity of zinc thrown down along with copper by sulphuretted hydrogen is not appreciable if the solution is sufficiently acid, but where great exactitude is required a double precipitation is recommended.

The complete separation of cadmium and zinc by sulphuretted hydrogen is impracticable, especially in presence of copper.

In separating arsenic from zinc, if the solution is distinctly acid, the zinc is not thrown down by sulphuretted hydrogen.

In separating iron and zinc the solution of the mixed metals should be poured drop by drop into the ammonia, and not *vice versa*. The zinc remains in solution and the precipitate is washed with ammoniacal water.

In separating manganese from zinc, the author acidifies with acetic acid and precipitates with sulphuretted hydrogen. All the manganese remains in solution.

CHAPTER VIII.

CADMIUM, GALLIUM, LEAD, THALLIUM, INDIUM, BISMUTH.

CADMIUM.

Estimation of Cadmium.

A VERY accurate and rapid process of estimating cadmium is based upon the reaction worked out by Leison.

Obtain the metal in the form of a strong aqueous solution as neutral as possible; add oxalic acid in excess, and then a large quantity of strong alcohol. The resulting oxalate is beautifully crystalline, and the precipitation is so complete that sulphuretted hydrogen gives a scarcely perceptible yellowish tinge in the filtrate. Wash the oxalate by Bunsen's method, and dry at 110°C. , until every trace of alcohol is expelled. Then pierce the filter with a glass rod, and wash the cadmium oxalate into a flask with hot dilute hydrochloric acid. A few c.c. of strong sulphuric acid are then added, and the hot solution is titrated with potassium permanganate. The results are very accurate. For further details on this method of analysis, see page 119.

A. Orłowski gives the following two methods for detecting cadmium in presence of copper in systematic qualitative analysis:—

Method I.—The blue liquid obtained after removal of the bismuth hydroxide is acidified with hydrochloric acid, and stannous chloride is added until the colour is destroyed. Milk of sulphur is then added, and the whole is heated to boiling. All the copper is thrown down as a black precipitate of copper sulphide. Filter, and add ammonia, when the tin is deposited as stannic and stannous hydroxide, whilst cadmium hydroxide, which is at first thrown down, is re-dissolved by the excess of ammonia. Filter again, and test the filtrate with hydrogen sulphide. A yellow precipitate indicates cadmium.

Method II.—The blue solution, after removal of bismuth hydroxide, is acidified with hydrochloric acid, mixed with sodium thiosulphate, boiled till the precipitate passes from a yellow to a dark brown (not black) and the liquid is colourless and transparent. If cadmium is present the characteristic yellow precipitate will appear on neutralising the filtrate with ammonia and adding ammonium sulphide. The second method is the simpler and better adapted for general use.

Separation of Cadmium from Copper.

Cadmium sulphide dissolves with the greatest facility in boiling dilute sulphuric acid, which has no action on copper sulphide. On precipitating by sulphuretted hydrogen a solution containing not more than 1 milligramme of cadmium mixed with 1000 milligrammes of copper, and boiling the black precipitate for a few seconds with dilute sulphuric acid (1 part concentrated acid and 5 parts of water), a colourless filtrate is obtained, in which an aqueous solution of sulphuretted hydrogen produces an unmistakable precipitate of yellow cadmium sulphide. Another solution of the same composition was mixed with an excess of potassium cyanide and treated with sulphuretted hydrogen gas. A distinct yellow colouration was observed: a deposit likewise took place, but so slowly that in delicacy the former experiment appears to have a considerable advantage, especially since a solution of *pure* copper in potassium cyanide also gives rise to a yellow colouration when submitted to the action of sulphuretted hydrogen.

Another method for the separation of cadmium from copper, due to Wöhler, is as follows:—Well wash the precipitated sulphides, and then dissolve them in hydrochloric acid, to which is added potassium chlorate. Precipitate the solution by an excess of potash, and dissolve the precipitate in hydrocyanic acid. This will form a solution of double cyanides, from which sulphuretted hydrogen precipitates the cadmium, but not the copper.

Another plan is to add to the solution of the two metals a considerable excess of tartaric acid, then a solution of caustic soda to alkaline reaction. Now dilute considerably and boil for some hours; the cadmium will be deposited. The filtrate containing the copper is then oxidised with aqua regia and precipitated with caustic potash.

Copper and cadmium may also be separated by precipitating the former with potassium sulphocyanide, after having first reduced it with sulphurous acid.

Mr. G. Vortman, for the separation of copper and cadmium, mixes the dilute solution (sulphuric or hydrochloric) of the metals with sodium thiosulphate till completely decolourised, and it is then heated to a boil, when the copper is separated as a heavy black sulphide. The boiling is continued till the liquid has become clear. After filtration and careful washing, the copper sulphide is mixed in the known manner with sulphur, and heated in a current of hydrogen. The cadmium in the filtrates is precipitated by one of the known methods.

E. Donath and J. Mayrhofer find that the statement of Ditte, that cadmium sulphide is appreciably soluble in ammonium sulphide, is unfounded. Cadmium sulphide, precipitated with ammonium sulphide, passes even through a double filter. Hence, sodium sulphide should be used if cadmium is present.

Separation of Cadmium from Mercury.

To the solution of the mixed metals add excess of hydrochloric acid and then phosphorous acid. This precipitates the mercury in the form of protochloride. Filter off, and to the filtrate add sodium carbonate, which will precipitate the cadmium as white carbonate. This is washed, dried, and converted by ignition into brown oxide. Care must be taken to remove as much of the precipitate from the filter as possible before calcining it.

Separation of Cadmium from Zinc.

Add a considerable excess of tartaric acid to the solution containing these two metals. Then add solution of caustic soda until the reaction is decidedly alkaline, and after dilution with much water keep the solution in a state of ebullition for several hours. Only the cadmium is deposited. The zinc may be separated from the filtrate by ammonium sulphide.

According to M. Kupfferschlaeger, a complete separation can be effected in a few hours by simply plunging a slip of bright zinc into the mixed solution in a test-tube, and leaving it there till all apparent action has ceased, decanting the liquid, washing the deposit of cadmium first with boiled water, and then with alcohol, drying with exclusion of air, and weighing. The author operates on a neutral solution of the sulphates, previously heated to expel the air. The test-tube is loosely stoppered.

Detection of Cadmium in Presence of Zinc before the Blowpipe.

Professor E. J. Chapman remarks that when cadmiferous zinc ores, or furnace products derived from these, are treated in powder with sodium carbonate on charcoal, the characteristic red-brown deposit of cadmium oxide is generally formed at the commencement of the experiment. If the blowing be continued too long, however, this deposit may be altogether obscured by a thick coating of zinc oxide. When, therefore, the presence of cadmium is suspected in the assay substance, it is advisable to employ the following process for its detection:—The substance, if in the metallic state, must first be gently roasted on a support of porcelain or other non-reducing body. Some of the resulting powder is then fused with borax or phosphor salt on a loop of platinum wire, and potassium bisulphate in several successive portions is added to the fused lead. The latter is then shaken off the wire into a small porcelain capsule, and heated with boiling water. A bead of alkaline sulphide is next prepared by fusing some potassium bisulphate on charcoal in a reducing flame, and removing the fused mass before it hardens. A portion of the solution in the capsule being tested with this, a yellow precipitate will be

produced if cadmium be present. The precipitate can be collected by decantation or filtration, and tested with some sodium carbonate on charcoal. This latter operation is necessary, because if either antimony or arsenic were present, an orange or yellow precipitate would also be produced by the alkaline sulphide. By treatment with sodium carbonate on charcoal, however, the true nature of the precipitate would be at once made known.

Detection of Cadmium in Presence of Metals whose Sulphides are Black.

Mr. T. Bayley proposes a method based on diffusion. The diluted solution is dropped upon filter-paper, and the spot allowed to extend as far as possible. On exposure to sulphuretted hydrogen, a black patch is formed surrounded by a vivid yellow ring. A solution containing much nickel, cobalt, or iron in presence of copper, &c., may be examined successively with sulphuretted hydrogen and ammonium sulphide. The presence of free acid increases the mobility of copper salts considerably.

GALLIUM.

Separation of Gallium from Cadmium.

This separation is effected only in an approximate manner by means of sulphuretted hydrogen. The difficulty is that in presence of a decided excess of hydrochloric acid the cadmium is not entirely precipitated, whilst if the solution is scarcely acid a portion of the gallium remains in the cadmium sulphide. Nevertheless, good results may be attained by a succession of operations, each of which yields a decreasing quantity of cadmium sulphide free from gallium. For this purpose a decidedly acid solution is treated with sulphuretted hydrogen, the precipitate is redissolved with hydrochloric acid, diluted with water, and again treated with sulphuretted hydrogen. This reaction, if repeated once or twice, enables us soon to collect the greater part of the cadmium as a sulphide free from gallium. The liquids which hold in solution all the gallium, along with a little cadmium, are concentrated to expel the large excess of acid, diluted with water, and saturated with sulphuretted hydrogen. The new deposit of cadmium sulphide obtained is dissolved and reprecipitated once or twice to free it from gallium. The repetition of this treatment frees the gallium chloride from every sensible trace of cadmium.

An excess of boiling potash precipitates cadmium oxide and dissolves gallium oxide, of which a small quantity remains in the cadmium oxide. It is therefore redissolved in hydrochloric acid and separated again by means of potash. When the cadmium is in a somewhat large proportion, 4 or 5 treatments are needful to extract all the gallium. The alkaline liquids contain merely feeble traces of cad-

mium; to separate these the liquid is supersaturated with a very slight excess of hydrochloric acid, and the gallium is removed by means of cupric hydrate. The filtered solution is mixed with a little ammonium acetate, and saturated with sulphuretted hydrogen, which precipitates copper and cadmium sulphides. These are taken up in aqua regia, evaporated with an excess of hydrochloric acid to destroy the nitric acid, and this very acid solution is then treated with sulphuretted hydrogen. The copper is thus eliminated, and we have merely to concentrate in order to obtain cadmium chloride.

The four following procedures are more expeditious :—

1. A prolonged boiling after supersaturation with ammonia precipitates gallium and leaves cadmium dissolved, but the original liquid should be very acid in order to form a sufficient quantity of ammonium chloride. The gallium oxide thus obtained retains very slight traces of cadmium, which are eliminated by a second similar treatment.

2. The separation can be effected well with potassium ferrocyanide, provided that the liquid contains about one-third of its volume of concentrated hydrochloric acid, which holds the cadmium ferrocyanide in solution.

3. Cupric hydrate, with the acid of heat, precipitates gallium containing scarcely a trace of cadmium, which a second operation entirely removes. This is an excellent process.

4. If it is required to remove iron at the same time as cadmium, the slightly acid liquid is reduced in heat by metallic copper, and is then mixed with a slight excess of cuprous oxide. The gallium oxide collected contains traces of cadmium which disappear on a repetition of the same treatment. The reaction of cupric hydrate and of metallic copper with cuprous oxide are the most to be recommended.

Separation of Gallium from Copper.

According to circumstances we may choose among the four following methods, all of which are good, but the first is to be preferred whenever applicable.

1. The hydrochloric solution, distinctly acid, is treated with a current of hydrogen sulphide. The copper sulphide is then treated with acidulated water containing hydrogen sulphide.

2. On ebullition, kept up for some minutes, potash throws down anhydrous cupric oxide containing no gallium. The separation is good.

3. In a solution kept slightly acid zinc easily throws down the copper without carrying the gallium along with it. It is much better to reduce the copper by means of the electrolysis of a sulphuric solution, quite free from chloride. The operation is performed in a platinum vessel, taking the precautions which the author gives for the electrolytic estimation of copper.

4. The separation may be effected by the prolonged boiling of a solution supersaturated with ammonia, provided that the copper is not very abundant, in which case the operation has to be several times repeated. The original hydrochloric solution must be very acid in order that it may afterwards contain a notable quantity of ammonium chloride.

Separation of Gallium from Mercury.

Of the three following methods the first must be especially recommended as exact and rapid.

1. The hydrochloric solution, distinctly acid, is treated with an excess of hydrogen sulphide.

2. The mercury may be reduced by zinc, or preferably by copper, in a liquid kept slightly acid. The reduction of mercury is more rapid than that of bismuth; it is complete, and the precipitate contains no gallium. The formation of a deposit of cuprous chloride is not an inconvenience.

3. Potassium ferrocyanide may be used for the separation of gallium from mercury in a very acid solution. The precipitate, if carefully washed with hydrochloric water, retains no mercury.

Chemical treatises generally teach that the precipitate formed by potash in mercuric salts is insoluble in an excess of the reagent. Nevertheless, potash cannot serve for the separation of gallium from mercury, since the alkaline liquid retains notable quantities of mercury. That part of the mercuric oxide which is precipitated on boiling is free from gallium.

Separation of Gallium from Silver.

1. In a very acid nitric solution the silver is removed by a slight excess of hydrochloric acid.

2. Sulphuretted hydrogen completely removes the silver contained in nitric solutions moderately acid, or in strongly acid hydrochloric liquids.

Separation of Gallium from Cobalt.

However slight the proportion of cobalt, caustic potash does not give very good results, in consequence of the relatively considerable entanglement of gallium in the oxide precipitated. Sensible traces of gallium may be detected in cobalt oxide which has been precipitated with excess of potash five times in succession, and this when operating upon a liquid containing merely 0.005 gramme gallium in 2 to 3 grammes of cobalt oxide. Yet, after the seventh potassic treatment, there no longer remains any gallium in the cobalt oxide. The process is therefore only fit for removing small quantities of cobalt mixed with much gallium; the small precipitate of cobalt oxide is then freed from the last traces of gallium by one of the other methods. The potassic filtrates often retain a trace of cobalt, which tinges them blue;

exposure to the air decolourises these solutions in one or two days in the cold, or in one hour with heat, brown cobalt oxide being deposited.

Barium and calcium carbonates effect at first merely an imperfect separation of gallium and cobalt. Even in the cold, after a contact of 6 hours, the precipitates contain notable quantities of cobalt oxide. Contrary to what happens with the zinc salts, a little more cobalt oxide is found in the precipitate with the calcium than in that with the barium salt. The inconvenience of the precipitation of a certain quantity of cobalt oxide in presence of barium and calcium carbonates is diminished by the separation which is naturally effected between gallium and cobalt, when boiling with ammonia or treatment with cupric hydrate are employed to eliminate calcium and barium salts.

In the reaction of calcium carbonate in heat, after sulphurous reduction, there are also deposited notable quantities of cobalt oxide, which, nevertheless, are entirely eliminated if the operation is repeated once or twice, and also on ammoniacal ebullition or treatment with copper hydrate for the removal of lime. Prolonged boiling after supersaturation with ammonia enables us to separate very conveniently gallium from cobalt. It is necessary to operate upon a very acid liquid, so as to produce a sufficient quantity of ammonium chloride, taking care to boil previously, so as to destroy the cobalt per-salts. The ammonia is not added until after the liquid has begun to boil. The purpureo-cobaltic salts, which are sometimes formed in small quantity, are dissolved and carried away in the washing waters. The gallium oxide thus obtained retains almost always traces of cobalt, which are eliminated on repeating the operation.

Excellent results are obtained either by means of cupric hydrate or of metallic copper and cuprous oxide. Sensible traces of cobalt, however, remain in the first copper precipitates; but they are easily removed by one, or at most two repetitions.

Separation of Gallium from Nickel.

Nickel oxide precipitated by an excess of boiling potash retains gallium more energetically than does cobalt oxide. With a liquid containing 0.005 gramme gallium and 2 to 3 grammes nickel oxide, a very notable proportion of the gallium is found in the precipitate after the seventh treatment with potash. This procedure is consequently applicable only in case of a small quantity of nickel mixed with much gallium. The galliferous nickel oxide is then analysed by one of the other procedures.

If we have mixtures containing little gallium and a large mass of protoxides, such as those of cobalt, nickel, manganese, zinc, &c., it is almost always very advantageous to begin by precipitating at a boil all the gallium sesquioxides by means of an alkali, along with a small fraction of the protoxides. The detection of the gallium becomes then easier, since it bears upon a small bulk of matter. The action of calcium and

barium carbonates in the cold, as well as that of calcium carbonate in heat after sulphurous reduction, require the same remarks as in the case of the separation from cobalt. It has likewise been found that a little more nickel oxide is rendered insoluble with calcium carbonate than with barium carbonate.

A good separation is obtained by boiling with ammonia. The original hydrochloric solution ought to be very acid. Especially if the nickel is abundant, the precipitate contains quantities of it not to be neglected. It is removed by repeating the same process once or twice. Cupric hydrate, as well as metallic copper and cuprous oxide, are excellent reagents to employ. The traces of nickel oxide carried down in the precipitates in the first operation are eliminated on repeating it once or twice.

Separation of Gallium from Manganese.

M. Lecoq de Boisbaudran has found the nine following methods effective :—

1. He treats the boiling liquid with an excess of aqueous potash. The precipitate contains a quantity of gallium, and is redissolved in hydrochloric acid and treated afresh with potash. This process is repeated four or five times; the alkaline solutions collected together are concentrated and filtered to separate a little brown manganese oxide. The gallium is removed from the alkaline salts by ebullition with ammonia, or with cupric hydrate. If the proportion of manganese is very considerable this process loses much of its advantage, because of the difficulty of washing completely the bulky deposits of manganese oxide.

2. The hydrochloric solution, distinctly acid, is kept at a boil for some minutes (which reduces the manganese per-salts); it is then supersaturated with ammonia, and boiled until it reddens litmus-paper; the water lost by evaporation is constantly replaced. The gallium oxide obtained sometimes retains traces of brown manganese oxide; it is then redissolved in hydrochloric acid, and the ammoniacal ebullition is repeated, taking care not to add the ammonia until the acid liquid has boiled for a few minutes.

3. Barium carbonate separates gallium in the cold in 12 to 18 hours, leaving manganese chloride dissolved. Traces of manganese may be found in the precipitate, but they are eliminated, after the separation of the barium and gallium, by means of boiling with ammonia or cupric hydrate.

4. Calcium carbonate may be used in the same manner as barium carbonate.

5. If iron is present, it is advisable to eliminate a good part of this metal at the same time as the manganese. For this purpose the hot acid liquid is reduced by sulphurous acid gas or sodium sulphite. After boiling for a few moments the author adds a small excess of

calcium carbonate, and filters. The separation of the calcium and gallium is effected in the ordinary manner. This method is especially useful in extracting gallium from its ores.

6. Cupric hydrate, applied hot, affords an excellent means for separating gallium from manganese. The process is conducted as has been previously described.

7. In presence of iron the liquid may be first reduced by metallic copper, and the gallium precipitated by means of the cuprous oxide. This process is as accurate as that with cupric hydrate.

8. When the quantity of gallium is very small in comparison with the mass of manganese salts, it is sometimes advantageous to use the reaction of arsenic sulphide formed in a solution supersaturated with acid ammonium acetate. Manganese sulphide is not formed under these conditions. The separation is very good.

9. The reaction of potassium ferrocyanide is applicable to the precipitation of gallium mixed with manganese compounds, but it is necessary to operate in an especial manner, for the presence of manganese chloride modifies the action of ferrocyanide upon gallium chloride. If we divide into two equal parts a very dilute and very acid solution (containing one-third of its volume of hydrochloric acid) of gallium chloride, and introduce into one of the halves manganese chloride, the addition of equally very small quantities of ferrocyanide produces very different effects in the two vessels. The solution of gallium alone becomes abundantly turbid, whilst the solution containing manganese remains at first clear, and then slowly deposits a reddish-brown precipitate which contains the gallium. This brown precipitate is redissolved if heated with its mother-liquid, and is slowly reproduced on cooling. The precipitate formed in the liquid free from manganese does not dissolve in its mother-liquid if raised to a boil, but it dissolves on heating if some manganese chloride is previously added to the mother-liquid. After cooling, the reddish-brown precipitate is then gradually produced.

If, instead of pouring very little prussiate into the solution of gallium and manganese, we add much, the brown precipitate is formed at once, but retains its property of being dissolved on heating and re-precipitated when cold.

If a clear, very acid solution, containing gallium chloride, an excess of manganese chloride, and ferrocyanide, is kept at a temperature of 70° to 80°, there is soon formed a turbidity, not brown, but white with a blue cast; it is in appearance the ordinary precipitate of gallium ferrocyanide, but it does not dissolve if heated with the excess of the manganese salt. This precipitate contains all the gallium. In the liquid, when cold, the deposit does not turn brown. By operating as follows an accurate separation of gallium and manganese can be effected with ferrocyanide.

The solution containing about one-third of its volume of concen-

trated hydrochloric acid is raised to 70° ; a quantity of ferrocyanide is then added, not too great, in order to avoid the formation of much Prussian blue, but still larger than if it was required to precipitate the same weight of gallium in the cold in presence of metals such as aluminium or chromium. The ferrocyanide should be neither too dilute, nor acidified with hydrochloric acid. Drops of moderately concentrated ferrocyanide give, on contact with the highly acid liquid, a white precipitate, which would be equally formed with hydrochloric acid alone, and which redissolves on stirring if the quantity of ferrocyanide is small. The momentary presence of this slight turbidity incites and accelerates the deposition of the gallium ferrocyanide. The liquid is stirred frequently, and is kept at about 70° for 30 to 60 minutes, then filtered, the deposit washed with water containing one-fourth hydrochloric acid, and heated to 70° . 0.001 gramme of gallium, corresponding to 0.0025 gramme of gallium chloride, may be recovered in this manner without appreciable loss, from 200 c.c. of a very acid solution containing 12.5 grammes of anhydrous manganese chloride. The limit of the sensibility of the process is not reached here, though the liquid contains merely $\frac{1}{50000}$ of gallium, and the gallium chloride bears to the manganese chloride the proportion 1 : 5000. If from deficient washing or otherwise the gallium ferrocyanide retains traces of manganese, these are naturally eliminated during the treatment necessary to separate gallium from iron, such as the boiling with ammonia of the product of the action of bisulphate upon the oxides, and the action of metallic copper and cuprous oxide.

Separation of Gallium from Uranium (Yellow Uranic Salts).

The four following methods are suitable for exact analyses:—

1. The hydrochloric solution, slightly acid, is treated at a boil with an excess of cupric hydrate. The deposit contains all the gallium as well as a very sensible portion of uranium. It is redissolved in hydrochloric acid, diluted with water, and boiled in presence of a large excess of cupric hydrate. With from 10 to 15 parts of uranium to 1 of gallium, four successive precipitations are required. The uranium is then entirely contained in the liquids which are acidified, and are then traversed by a current of sulphuretted hydrogen. Copper sulphide is deposited, and the uranium salt is obtained on evaporating the filtrate.

2. If there is iron to remove along with uranium, it is first reduced hot with metallic copper and then boiled with an excess of cuprous oxide. Four successive operations suffice to separate completely 1 part of gallium from 10 to 15 parts uranium. The presence of very considerable quantities of alkaline salts does not interfere with the execution of the two methods just described, which may serve for the analysis of a mixture of gallium and of an alkaline uranate.

3. The hydrochloric solution, slightly acid, is mixed with an

excess of acid ammonium acetate, as also a certain quantity of zinc free from gallium, and is then treated with a current of sulphuretted hydrogen. The zinc sulphide carries down the gallium, whilst the uranium remains in solution; only the zinc sulphide, being very difficult to wash, ought to be redissolved in hydrochloric acid and re-precipitated in an acetic solution. The gallium is separated from zinc by boiling its solution in hydrochloric acid with excess of ammonia. The uranium is separated by evaporating the liquids with an excess of hydrochloric acid to expel acetic acid, and then destroying the ammoniacal salts with aqua regia. It is essential to add to the liquid so much zinc chloride that the zinc sulphide may carry down all the gallium. Some drops of zinc chloride should be added to the filtered hydrosulphuretted liquids to ascertain the absence of gallium in this last zinc sulphide. Alkaline salts do not interfere with the separation of uranium and gallium by means of zinc sulphide. The present process is suitable for the detection of small traces of gallium in large masses of uranic compounds, especially in presence of metals such as aluminium. But in ordinary cases it is better to make use of the reactions of copper hydrate or of metallic copper and cuprous oxide.

4. Uranium may be precipitated by a slight excess of caustic potash as an alkaline uranate, scarcely retaining a slight trace of gallium, which may be entirely removed by redissolving in hydrochloric acid and re-precipitating with potash. The alkaline liquids collected contain all the gallium and traces of uranium. These liquids are slightly supersaturated with hydrochloric acid, mixed with an excess of cupric hydrate, and raised to a boil, when the gallium is completely precipitated. In the filtrate, copper, uranium, and potassium are separated by known methods. When the potash employed contains a little carbonate (a frequent case) the proportion of uranium not precipitated is sensibly increased; this is without inconvenience, since the separation of this gallium and of the dissolved uranium is effected afterwards by the action of cupric hydrate.

LEAD.

Preparation of Pure Lead.

As in the case of silver, the most valuable information on the subject of the purification of metallic lead is due to the researches of Professor Stas on the relations existing between atomic weights. The preparation of pure lead offers even more difficulties than that of pure silver.

In the following pages are given those processes which yielded the best results.

Preparation of Lead by reducing the Carbonate with Potassium Cyanide.—Commercial lead acetate was dissolved in warm water, contained in a large leaden digester, and kept at a temperature

of 40° to 50° in contact with very thin sheets of lead until all the copper and silver were precipitated. The solution was then filtered and poured into nearly boiling water, strongly acidulated with sulphuric acid. The lead sulphate was washed by decantation until the washing waters contained no trace of sulphuric acid. The salt was then transformed into carbonate by means of a mixture of ammonium sesquicarbonate and solution of ammonia; for this it is only needful to diffuse it in the water containing the alkaline salt; an effervescence takes place, which lasts as long as there remains lead sulphate undecomposed. At this point the solution of ammonium sulphate and the excess of ammonium carbonate is decanted, and the precipitate washed with pure water as long as the washing waters contain sulphate in solution.

The lead carbonate thus formed dissolves entirely in dilute nitric acid. It is perfectly free from foreign metals, except traces of iron, which adhere to the lead sulphate in spite of the excess of sulphuric acid employed. To separate the iron, transform a portion of this lead carbonate into oxide, by heating it carefully in a platinum vessel. Another portion is dissolved in dilute nitric acid, taking the precaution to leave some of the carbonate undissolved. The solution of nitrate is heated to ebullition and the lead oxide then gradually added to it. The oxide in dissolving precipitates traces of iron. The liquid is filtered and an excess of ammonium sesquicarbonate poured into it. In the lead carbonate thus obtained it is impossible to discover the slightest trace of foreign metal. It is this carbonate which is converted into metallic lead. To effect this, after having dried it, project it, by small quantities at a time, into pure fused potassium cyanide. As this reduction ought to be effected in a white, unglazed porcelain crucible, which is very liable to break, recourse may be had to the same plan which was used in the reduction of silver from its chloride, and in the fusion of the pure metal (page 278)—that is to say, fix the porcelain crucible in the centre of another larger one, interposing between them calcined pipeclay, which has been reduced to powder, cementing the whole together by the addition of 5 per cent. of fused and powdered borax.

The lead obtained by the first operation is heated a second time with pure potassium cyanide until it presents at the bottom of the cyanide a surface as convex and brilliant as pure mercury. When it is somewhat cool, cast it in a polished ingot-mould of cast steel.

When the lead contains the slightest trace of oxide or sulphide it does not present a convex surface when it is fused.

Pure lead is much whiter and more soft than the ordinary metal. It appears to tarnish very rapidly when exposed to the air.

Preparation of Lead by reducing the Carbonate by Black Flux.—Instead of reducing the lead carbonate by potassium cyanide, black flux obtained by carbonising purified Seignette salt may be

employed. To entirely deprive this salt of foreign metals, first pass a current of hydrosulphuric acid through its boiling solution ; then pour in a few drops of sodium sulphide solution. The coloured solution, left to itself for 15 days in a well-stoppered bottle, becomes completely decolourised by depositing the metallic sulphides. The decanted solution is agitated with lead tartate as long as it contains the slightest trace of sodium sulphide. Before calcining the Seignette salt, it should always be tested to see that it contains neither sulphide, sulphate, nor foreign metals.

The lead carbonate mixed with the pulverised black flux is reduced by the action of heat. The temperature necessary for the fusion of the alkali being tolerably high, there is almost always a certain quantity of alkaline metals reduced which alloy with the lead. To remove these metals, heat the lead for some time in contact with the air, continually stirring the metallic bath with a rod of pipeclay. When a certain quantity of the lead has been thus oxidised, pour on the mass fused potassium cyanide, and heat the whole until a great portion of the cyanide is volatilised. The lead is then allowed to cool to near its point of solidification, and then run into an ingot-mould of polished steel.

Preparation of Lead by reducing the Chloride.—Treat with an excess of dilute hydrochloric acid the lead carbonate prepared by the action of ammonium sesquicarbonate upon the lead sulphate. The minute traces of iron contained in the carbonate remain dissolved in the excess of hydrochloric acid. Two different plans may be used to reduce the chloride. One consists in mixing it with two-thirds of its weight of pure sodium carbonate and projecting the intimate mixture into fused potassium cyanide. The metallic lead produced is poured into another crucible with a fresh quantity of pure fused potassium cyanide. It is there kept at a high temperature and continually agitated until the surface, flat and dull as it is at first, becomes strongly convex and brilliant. When sufficiently cool it is poured into an ingot-mould and kept away from moist air.

The other plan for reducing the chloride consists in heating an intimate mixture of it with sodium carbonate and black flux. The resulting lead is fused and agitated for some time in contact with air, and then heated with cyanide to remove the last traces of oxide.

Estimation of Lead by Precipitation in the Metallic State.

To estimate lead by this method, M. F. Stolba treats both soluble and insoluble lead combinations with zinc in the presence of water acidulated from time to time with hydrochloric acid ; the reduction is effected at the temperature of the water-bath in a platinum capsule ; the lead is deposited partly on the sides of the capsule and partly on the zinc, whence it is easily dislodged. When the reduction is complete, which is easily discerned by a clean surface of the zinc remaining

brilliant in the liquid, decant and wash the spongy deposit of lead with water. As pure water might oxidise and dissolve small quantities of lead, an addition of a drop of sulphuric acid is advisable. After washing, dry the lead first in a water-bath, then at about 200° C. Its exact weight cannot then be ascertained because it has undergone a partial oxidation. After weighing it the amount of oxygen absorbed must be ascertained, which may be done by treating the lead with a weak standard solution of nitric acid. Wash the lead from dissolved oxide, and to the acid solution add a standard alkaline solution until it begins to produce turbidity. The quantity of lead oxide is given by the difference in the standard of the nitric acid before and after its action on the lead.

Precipitation of Lead as Sulphate.

The estimation of lead in the state of sulphate, by means of sulphuric acid and evaporating to dryness, insures accuracy, but the process requires constant attention. Towards the end of the analysis the evaporation exposes it to loss by projection; moreover, if the liquids contain iron, the lead sulphate is often contaminated with the slightly soluble ferric sulphate. The solubility of lead sulphate, even in water, is well known, as the following experiment shows:—Precipitate 1 equivalent of lead nitrate by 2 equivalents of sulphuric acid diluted largely with water; then wash during several days, and long after the washings have ceased to reddens litmus-paper, they will still become slightly turbid by barium nitrate and ammonium sulphide.

The use of soluble sulphates, suggested by various authors, M. Levol has shown is not to be recommended.

The first impression was, that the principal inconvenience arose from the incomplete insolubility of lead sulphate, and that, consequently, the employment of alkaline sulphates would produce but imperfect results. But it appears that, under these circumstances, there is an overweight in precipitating lead by potassium sulphate. If, in fact, liquids much charged with lead nitrate and potassium or sodium sulphate in excess are put in contact, precipitates are obtained the weight of which considerably exceeds that of the lead sulphate corresponding to the weight of nitrate; and it is with difficulty that they are reduced to this weight by washing.

From careful analyses, it appears that there are formed by the wet way, under certain conditions, double lead and potassium or sodium sulphates, and in a paper published in 1825 by Tromsdorff it is pointed out that the potassic salt is obtainable by the precipitation of lead acetate by potassium sulphate. He also adds that by boiling this salt with a large quantity of water, the proportion of potassium sulphate which it contains gradually diminishes.

It is only under particular conditions of concentration of the liquids that these salts can be formed, but, on the whole, experience shows

that alkaline sulphates should not be employed in the estimation of lead in the state of sulphate, if the precipitate is weighed, partly because of the danger about to be described, and partly because of the fear of loss of lead sulphate by the numerous washings necessitated by the decomposition of the double salts by water.

Mr. H. C. Debbits finds that lead sulphate is soluble in sodium, calcium, manganese, zinc, nickel, and copper acetates. The mercury and silver acetates have no such solvent action. The barium acetate at common temperatures partially converts the lead sulphate into lead acetate and barium sulphate; the inverse reaction does not take place.

S. Rovera, whilst examining quinine citrate for an admixture of quinine sulphate, observed that lead in presence of ammonium citrate is not precipitated from an alkaline solution by sulphuric acid, or an alkaline sulphate. It is, however, completely precipitated by potassium or sodium carbonate.

Estimation of Lead as Carbonate.

In face of the difficulties to be encountered in estimating lead with great accuracy, it appears advisable that it should be estimated in the state of carbonate, and for that purpose ordinary ammonium carbonate, to which is added caustic ammonia, should be used. The object of this addition is to avoid the employment of too large a volume of solution of ammonium carbonate, a salt not very soluble in water. Ammonia forms, with lead nitrate for instance, a very incomplete precipitate. It would not, then, be prudent to divide the operation into two—that is to say, to employ ammonia first to saturate the liquid—and, consequently, it should not be poured in until it has been charged with ammonium carbonate, which it dissolves abundantly and easily. The precipitate separates perfectly from the liquid, is easily collected and dried on a filter. The deposition of the precipitate is completed in about 24 hours, especially under the influence of gentle heat. Two or three parts of lead in a thousand can be estimated by this process.

The precipitate, which is the anhydrous monocarbonate, is deposited on a small double filter, each one of the same weight.

If, as frequently happens in analysing metallic substances, the colour, which should be pure white, is yellowish, it is owing to the presence of iron, which is easily got rid of by washing the filter with water acidulated with sulphuric acid after weighing.

If there is reason to suspect the presence of bismuth, treat a small quantity of the weighed precipitate by a little nitric acid. A few drops of potassium iodide in the liquid will detect the presence of bismuth by the forming of a brown precipitate, or yellow-brown if there is bismuth and lead. The latter metal, when present alone, gives a pure yellow precipitate. (See also Separation of Bismuth from Lead.)

Estimation of Lead as Iodate.

Dr. C. A. Cameron finds that lead iodate is practically insoluble. Iodic acid and alkaline iodates precipitate lead far more perfectly than sulphuric acid, even when alcohol is added to the latter. The plumbic iodate formed is weighed, or, if a volumetrical method be desired the following is the process :—Precipitate with standard solution of soluble iodate, and filter off the plumbic iodate. The filtrate and washings are to be mixed, and the excess of iodic acid contained in them estimated volumetrically by the hydrochloric acid and thio-sulphate method. As it is almost impossible to procure pure iodic acid or potassium iodate, the solution of iodate must be standardised by means of a solution of pure lead nitrate. Owing to the slight solubility of plumbic iodate in alkaline chlorides, iodides and bromides, none of these salts must be present. Hydrochloric acid rapidly dissolves lead iodate.

Precipitation of Lead by Oxalic Acid.

It has already been stated that in estimating lead by ammonium carbonate in presence of an excess of ammonia, two or three parts of this metal in a thousand can be estimated. By operating, under the same conditions, with oxalic acid, it is impossible to estimate it to less than 1 per cent. It has been observed that the precipitation of lead by oxalic acid should be effected in neutral solutions; but this necessity ill agrees with the most ordinary instances of the analysis of metallic substances, where the presence of an excess of ammonia is indispensable for maintaining in solution certain substances from which the lead requires to be separated.

Detection and Estimation of Small Quantities of Lead in the Presence of other Metals.

The separation of lead from its solutions and from other metals by means of potassium chromate does not appear to have attracted the attention of analytical chemists to the extent which it merits, judging from the published special methods of analysis which include the estimation or detection of that metal.

There are frequent instances in which the potassium chromate offers considerable advantage as a precipitant of lead over hydrosulphuric or sulphuric acids, the two reagents in general use, more particularly for the detection of minute quantities. The efficiency of this reagent is, moreover, much increased by the circumstance that lead chromate is all but insoluble in acetic acid. It is, indeed, one of the most insoluble of the lead salts, and has, therefore, claim to superiority over the more soluble sulphate; whilst the scarcity of insoluble chromates renders potassium chromate valuable for effecting the separation of lead from other metals in cases where the reagents referred to are inapplicable. The precipitation of lead in the presence

of copper, for example, is more readily effected by the addition of potassium bichromate to an acetic solution; a trace of lead which would otherwise escape detection is rendered evident after a time by the deposition of the characteristic yellow precipitate.

Potassium bichromate in the presence of free acetic acid is also applicable as a means of separating small quantities of lead from zinc (*i.e.* in the analysis of the spelters in commerce). The precipitation of lead by hydrosulphuric acid from the hydrochloric solution is at times anything but satisfactory; the solubility of the lead sulphide in the excess of hydrochloric acid which must be employed to prevent the precipitation of the zinc is sufficient to lead frequently to the belief that lead is absent when it really exists in the spelter to a very appreciable amount. (It may be observed that this liability to error, in the use of hydrosulphuric acid, is not nearly so great when nitric acid is employed.)

If much bismuth be present in the substance under examination, some bismuth chromate will be precipitated, together with the lead. In such instances the separation of the two metals must be effected by a special method.

The lead chromate, when freshly precipitated from a cold solution, is sometimes difficult to separate perfectly from the liquid by filtration; this is not the case, however, if the precipitate is allowed to stand for some time, or if it is produced in a hot solution.

The most accurate way of estimating the weight of minute quantities of lead precipitated as chromate is to convert the metal finally into sulphate. For this purpose the chromate is dissolved in a little hot dilute hydrochloric acid; a small crystal of tartaric acid is added, and the solution, rendered alkaline by ammonia, is treated with hydrosulphuric acid, or mixed with a few drops of ammonium sulphide. The lead sulphide thus obtained is washed and converted into sulphate by the usual method.

Volumetric Estimation of Lead.

M. Graeger estimates lead with potassium ferrocyanide.

Lead ferrocyanide is almost insoluble in acids, and its precipitation is easy. The author employs a standard solution of potassium ferrocyanide; when all the lead is precipitated, the liquid colours ferric salts blue, which may be tested in one drop of it. An excess of ferrocyanide may be added, and estimated in the filtered liquid by potassium permanganate. As a control, the lead ferrocyanide may be suspended in water and titrated by permanganate.

Volumetric Estimation of Lead by Precipitation as Chromate.

Some years ago Dr. H. Schwarz published a process for the volumetric estimation of lead which consisted in precipitating a lead solution (acidulated with nitric acid) by means of an excess of potas-

sium bichromate ; the precipitate when subsided had to be washed and filtered and precipitate and filter placed in a freshly-prepared standard solution of iron protochloride. Decomposition took place, the chromic acid was reduced to the state of oxide, and the lead converted into and dissolved as chloride. When filtered and washed, the remaining undecomposed iron protochloride was estimated by potassium permanganate, and from the difference between the remaining and original amount of iron the quantity of chromic acid was calculated, and in this way the amount of lead ascertained. This process, while it gives accurate results, requires, like that devised by Hempel, two filtrations and washings.

The following process is more simple :—Dissolve 14·730 grammes of pure potassium bichromate in sufficient water to form 1 litre. One cubic centimetre of this solution precipitates 0·0207 gramme of lead.

In the analysis of metallic lead, a certain quantity should be dissolved in a minimum of nitric acid, the solution diluted with water, carefully neutralised with ammonia or sodium carbonate, an excess of sodium acetate added, and the solution precipitated by the potassium bichromate solution. When the precipitation approaches its end, or when the precipitate commences readily to subside, some drops of a neutral solution of silver nitrate are spread out on a porcelain plate, and the potassium chromate solution only added by 2 or 3 drops at a time to the liquid under examination : after each addition the whole is well stirred, allowed to subside, and the silver solution on the plate touched with a drop of the clear supernatant liquor. As soon as the potassium bichromate is in excess the two drops form a red colour, while the precipitated lead chromate has no effect on the silver test, but simply floats on the top as a yellow precipitate. Should the solution assume a yellow colour before the silver reaction has commenced, it would indicate that not sufficient sodium acetate had been added in the first instance, and it would be necessary to add this now, and also a c.c. of a normal lead solution, containing 0·0207 of lead as nitrate. The slight turbidity which first takes place soon goes off, and the operation may be proceeded with as before. One c.c. must, of course, in this case, be deducted from the amount of chrome solution on account of the extra addition of lead.

Of all foreign metals bismuth alone seems to interfere with the reaction ; it behaves very like lead with chromic acid, and, if present, necessitates a different mode of proceeding. Tin and antimony are converted into insoluble oxides during the solution of the lead in nitric acid. Arsenious acid offers no difficulties, but lead arseniate is insoluble in an acetic solution, and is only partly decomposed by potassium bichromate, consequently its removal becomes necessary. Gold and platinum are insoluble in nitric acid.

The presence of silver is of no great importance ; during the operation the lead is first thrown down as a yellow precipitate, and after-

wards the precipitation of the silver takes place, giving the red reaction similar to the silver test always resorted to. It may, however, be separated from the lead solution by means of sodium chloride, and the silver chloride either filtered off, or in case not much excess of sodium chloride has been used, left in the solution, and the lead estimated as usual. Lead chloride is tolerably soluble in hot water, and lead chromate is not decomposed by sodium chloride, although this salt decomposes silver chromate.

The higher mercury oxide is not precipitated by potassium bichromate, not even in an acetic solution, while the lower oxide is; and, as it is difficult to peroxidise all the mercury when amalgamated with lead, even by long-continued boiling in nitric acid, it becomes necessary to evaporate and calcine the residue till all the mercury is volatilised. To obviate the formation of lead peroxide, the calcined residue must be moistened with a few drops of oxalic acid, and again dried and carefully calcined and dissolved in acetic acid; after this, the lead may be estimated as usual. To avoid the above calcinations the mercury may be precipitated from the nitric acid solution by means of hydrochloric acid, and the calomel boiled till converted into mercuric chloride.

Copper, cadmium, zinc, iron, and cobalt do not in the least interfere with the reaction, provided the iron is peroxidised. Of the different acids, hydrochloric acid somewhat disturbs the last silver reaction, but by using larger drops, and allowing the reaction of silver chloride to go off, the usual silver chromate reaction is obtained.

Lead sulphate has first to be converted into the state of carbonate by boiling with sodium carbonate, when it may be dissolved in acetic acid. Lead phosphate and arsenite, or other lead salts insoluble in acetic acid, may be dissolved in nitric acid, and estimated according to Dr. Schwarz's original method.

M. Binsson's method is based on the precipitation of lead by potassium bichromate in excess; the excess of the bichromate employed is found by decomposing it in the cold by potassium iodide in presence of sulphuric acid. The reaction is almost instantaneous at common temperatures, and is complete in 2 or 3 minutes. The iodine set at liberty is estimated with sodium thiosulphate as indicator: either the disappearance of the blue tint of the starch iodide or the decolouration of iodine in carbon disulphide may be made use of. The author prefers the latter, as being much the more sensitive, for the liquid being always tinged greenish by the chrome salt produced, the sensibility of the reaction of starch is much lessened. The standard solution of bichromate is prepared by dissolving in distilled water 14.248 grammes pure fused potassium bichromate, and making the solution up to 1 litre: 5 c.c. precipitate exactly 0.1 gramme lead. The relation between the standard liquids of bichromate and thiosulphate is thus estimated. With a pipette, 25 c.c. of the bichromate

liquid are taken and diluted with water to 250 c.c. Of this new solution 50 c.c. are taken and put into a stoppered bottle capable of holding 250 to 300 c.c. The liquid is then acidulated with sulphuric acid (free from chlorine and nitrous vapours), and about 0.5 gramme potassium iodide is added. When the decomposition is effected about 5 c.c. carbon disulphide or chloroform is added. The solution of thiosulphate is then added by means of a burette graduated in $\frac{1}{10}$ of a c.c., until the rose colour of the carbon disulphide disappears: the quantity of thiosulphate added corresponds to 5 c.c. of bichromate or 0.1 gramme of lead. The solution of thiosulphate is sufficiently strong if from 35 to 40 c.c. are required to decolourise the iodine set at liberty by 5 c.c. of bichromate. The sulphuric acid should not be added in too large excess, as it might decompose the thiosulphate before the latter can act upon the iodine. In order to verify the standard of the bichromate, 0.8 gramme of pure lead is dissolved in pure hot nitric acid, for which purpose there are required about 20 drops of acid in 5 c.c. of water. When the lead is dissolved the liquid is heated to a boil to expel nitrous vapours, and the excess of acid is saturated with potash until a permanent precipitate is obtained, which is then redissolved by a few drops of acetic acid. The solution of lead is poured into a graduated flask of 250 c.c. with 25 c.c. of the bichromate solution, and distilled water enough to make up the 250 c.c. After standing for 15 minutes, the liquid is poured upon a dry filter, and the operation is completed in the same manner as if the bichromate alone were present, as described above. The difference between the quantities of thiosulphate employed for decomposing the bichromate before and after the partial precipitation by lead represents the bichromate in c.c. of thiosulphate, and consequently the lead which has been precipitated. For the assay of lead ores, the sample is ground in an agate mortar, and from 0.5 to 1 gramme, or more, is weighed out according to its richness. The weighed portion is dissolved in a few c.c. of boiling hydrochloric acid, and a little potassium chlorate is then added to peroxidise the iron, and the whole is boiled for a few minutes to expel chlorine. The liquid is then saturated with an excess of caustic potash, and the precipitate is redissolved in a few drops of acetic acid. It is then boiled again to precipitate the iron and add the solution of the lead sulphate if any has been produced. The solution is filtered and the precipitate is washed in boiling water. To the cold liquid there are added 25 c.c. of bichromate and water, so as to make up 250 c.c. After settling for 15 minutes, the liquid is poured upon a dry filter. 50 c.c. of the filtrate are taken and treated as described above.

Assay of Galena in the Wet Way.

When in contact with metallic zinc, galena is readily decomposed by acids. Even oxalic, acetic, and dilute sulphuric acids are capable, when hot, of decomposing galena—metallic lead being deposited and

sulphuretted hydrogen gas set free—while with hydrochloric acid the decomposition is peculiarly rapid and complete.

Galena is easily decomposed, also, even in the cold by dilute nitric acid in presence of zinc; but the reaction differs in this case from that just described—not metallic lead but free sulphur is deposited, while lead nitrate goes into solution.

The reaction with zinc and hydrochloric acid has been employed with advantage by Mr. F. H. Storer, Professor of Chemistry in the Massachusetts Institute of Technology, for assaying galena, particularly the common American variety, which contains no other heavy metal besides lead. The details of the process are as follows:—Weigh out 2 or 3 grammes or more of the finely powdered galena. Place the powder in a tall beaker, together with a smooth lump of pure metallic zinc. Pour upon the mixed mineral and metal 100 or 150 c.c. of dilute hydrochloric acid which has been previously warmed to 40° or 50° C.; cover the beaker with a watch-glass or broad funnel, and put it in a moderately warm place.

Hydrochloric acid fit for the purpose may be prepared by diluting 1 volume of the ordinary commercial acid with 4 volumes of water. For the quantity of galena above indicated, the lumps of zinc should be about 1 inch in diameter by $\frac{1}{4}$ of an inch thick; they may be readily obtained by dropping melted zinc upon a smooth surface of wood or metal.

The zinc and acid should be allowed to act upon the mineral during 15 or 20 minutes in order to ensure complete decomposition. Any particles of galena which may be thrown up against the cover or sides of the beaker should, of course, be washed back into the liquid. It is well, moreover, to stir the mixture from time to time with a glass rod.

When all the galena has been decomposed, as may be determined by the facts that the liquid has become clear, and that no more sulphuretted hydrogen is evolved, decant the liquid from the beaker into a tolerably large filter of smooth paper, in which a small piece of metallic zinc has been placed. Wash the lead and zinc in the beaker as quickly as possible with hot water, by decantation, until the liquid from the filter ceases to give an acid reaction with litmus-paper; then transfer the lead from the beaker to a weighed porcelain crucible. In order to remove any portions of lead which adhere to the lump of zinc, the latter may be rubbed gently with a glass rod, and afterwards with the finger or a piece of caoutchouc, if need be. Wash out the filter into an evaporating-dish, remove the fragment of zinc, and add the particles of lead thus collected to the contents of the crucible. Finally, dry the lead at a moderate heat in a current of ordinary illuminating gas, and weigh.

The lead may be conveniently dried by placing the crucible which contains it in a small cylindrical air-bath of Rammelsberg's pattern,

provided with inlet and outlet tubes of glass, reaching almost to the bottom of the bath.

When the process is conducted as above described, the lead undergoes no oxidation; hence there is no occasion for igniting the precipitate in a reducing gas. The precipitate needs only to be dried out of contact with the air.

If desirable, the sulphur in the galena could be estimated at the same time as the lead, by arresting the sulphuretted hydrogen in the ordinary way.

If the mineral to be analysed is contaminated with a siliceous or other insoluble gangue, the metallic lead may be dissolved in dilute nitric acid after weighing, and the insoluble impurity collected and weighed by itself. In the case of galenas which contain silver, antimony, copper, or other metals, precipitable by zinc, the proportion of each metal must be estimated by assay or analysis in the usual way after the total weight of the precipitated metals has been taken.

Besides galena, almost any of the ordinary lead compounds may evidently be assayed by the method above described. For example, metallic lead may be precipitated quickly and completely from the sulphate, chromate, nitrate, oxide, and carbonate—and with peculiar ease from the chloride—by means of zinc and hydrochloric acid. The method would also furnish an easy qualitative test for the detection of baryta in whitelead. When applied to the analysis of lead nitrate, it would probably be best to decompose the nitrate by means of a solution of sodium chloride before adding the zinc and hydrochloric acid.

Estimation of Silver in Galena.

According to the supposed proportion of silver mix from 8 to 5 grammes of the ore, finely powdered, with 8 to 4 times their weight of a flux made up of equal parts of soda and saltpetre. Introduce the mixture into a porcelain crucible of suitable size, covered, and heat over the lamp till the contents are melted, when the mixture is thoroughly stirred up with a glass rod. It is then allowed to cool, and the crucible is placed in a capsule partly filled with water. Remove the softened metal from the crucible into the capsule, heat over a lamp, and filter the aqueous solution. Wash well the residue on the filter, rinse back into the same capsule, mix with dilute nitric acid, and evaporate to dryness; take up the dry residue in water acidulated with nitric acid, heat over a lamp, and filter into a flask, washing well with hot water. Allow the filtrate to cool in the flask, mix with ferric sulphate or iron-alum, and titrate with a solution of ammonium sulphocyanide according to Volhard's process, 1 c.c. of the solution representing 1 milligramme silver. The presence of small quantities of copper is not objectionable; lead is even advantageous, as the lead sulphate which is deposited shows the approach of the final reaction. Large proportions of iron interfere with the accuracy of the process.

The treatment of galena with nitric acid does not effect the complete solution of the silver present.

In all these cases the decomposition of the lead salt by the zinc is so complete that no trace of colouration is produced when sulphuretted hydrogen is added to the liquid decanted from the metallic lead.

Attempts to estimate sulphur and lead in the same portion of galena, by means of the reaction of zinc and dilute nitric acid above described, give no satisfactory results. The free sulphur obtained by treating galena with zinc and ordinary nitric acid, diluted with 8, 4, and 5 volumes of water, always retains a small quantity of lead, while a certain amount of sulphuric acid is found in the clear liquid. It is, in short, well-nigh or quite impossible to avoid the secondary reactions between zinc and lead nitrate, and between sulphur and nitric acid, which set in as soon as, or just before, the last traces of the galena have been decomposed.

Dr. F. Mohr estimates lead in galena as follows:—Two grammes finely powdered galena are placed in a small porcelain pan furnished with a handle. It is covered with ordinary pure hydrochloric acid, covered with a convex glass, heated to expel hydrogen sulphide and boiled. Much lead chloride separates out. When the acid is saturated with lead chloride, a small ball of zinc is added. A brisk escape of hydrogen ensues, and lead is deposited on the zinc. A gentle heat is applied until the liquid becomes clear and colourless, and the escape of hydrogen sulphide ceases. The liquid is poured off, and the lead is well washed with pure water in the capsule. Dilute nitric acid is poured upon the moist lead, and heat is applied till the metal is dissolved. The lead nitrate is dissolved, if needful, by the addition of water and the application of heat; the liquid is filtered and the filter washed with hot water. In the filtrate the lead is thrown down by the addition of dilute sulphuric acid in excess and heated for a time, when lead sulphate is deposited. The whole is filtered, the precipitate is washed with dilute sulphuric acid, and lastly with a little alcohol, dried, and the weight of the lead sulphate is found after incineration of the filter. The filter, when saturated with ammonia, shows scarcely a trace of brown colouration with sulphuretted hydrogen.

Estimation of Lead in Ores.

Mr. Lowe having observed that the aqueous solution of sodium thiosulphate is capable of dissolving lead sulphate, proposes to utilise this reaction for removing this salt from siliceous residual matter. Such residues, perfectly washed and separated from the filter, are stirred up in a suitable vessel with a cold concentrated solution of sodium thiosulphate. It is allowed to settle for some time, washed by decantation, and the residue stirred up afresh with a further quantity of the same solution. This operation having been repeated 2 or 3 times, the solutions are mixed together, and the lead is separated by means

of sulphuretted hydrogen or ammonium hydrosulphate. The lead sulphide thus obtained is further treated in the usual manner.

Detection of Lead Peroxide in Litharge.

Heat the litharge in a test-tube with sodium chloride and potassium bisulphate, and introduce into the tube a slip of paper coloured with a solution of indigo. If any peroxide be present chlorine is disengaged, which bleaches the paper.

Estimation of the Value of Lead Peroxide.

H. Fleck places a weighed quantity in a small flask fitted with a gas-delivery tube, and decomposes with dilute hydrochloric acid. The chlorine evolved is passed into a solution of potassium iodide. When the escape of gas has ceased the solution is titrated with sodium thiosulphate, and the percentage of lead peroxide is calculated from the quantity of iodine. In rich samples the moisture should be estimated specially.

Detection of Lead in the Tin Linings of Vessels.

M. Fordoz places, by means of a tube dipped in pure nitric acid, a slight layer of acid upon any part of the tinning, selecting by preference the thickest parts. Both metals are attacked, forming stannic oxide and lead nitrate. After a few minutes, heat slightly to expel the last traces of acid and allow to cool, then touch the pulverulent spot produced by the acid with a tube dipped in a solution of 5 parts of potassium iodide in 100 of water. The iodide has no action upon the tin oxide, but with the lead nitrate it reacts, forming yellow lead iodide, and showing the presence of even a small quantity of this metal. The surface of the tinning must be carefully cleaned before applying the nitric acid, and the acid should not penetrate to the iron or copper which forms the body of the vessel, as the reaction might thus be complicated.

Detection of Lead in Tin Paper.

A drop of concentrated acetic acid is let fall upon the suspected leaf, and a drop of a solution of potassium iodide is added. If there is lead present there is formed in 2 or 3 minutes a yellowish spot of lead iodide. Kopp moistens the leaf to be examined with sulphuric acid. If the tin is pure the spot remains white, but if lead is present there is formed a black spot.

Separation of Lead from Copper.

Supposing the two metals to be present in a nearly neutral solution, acidulate with acetic acid and add a solution of potassium bichromate. A yellow precipitate of lead chromate falls down which is insoluble in acetic acid. If only a trace of lead be present the precipitation will not take place immediately. Should the original solution contain free

mineral acid, an excess of sodium acetate must be added instead of acetic acid. For quantitative purposes the precipitated lead chromate is best converted into sulphate before weighing (see page 846).

Separation of Lead from Mercury.

Rose's method of precipitating mercury protochloride from the solution by the addition of hydrochloric acid and phosphorous acid, is not applicable to the separation of mercury and lead. A portion of the lead is precipitated in the state of chloride with the mercury protochloride. A better plan for analysing a mixture of the salts of these two metals is to add sulphuric acid, and then alcohol forming about $\frac{1}{2}$ of the volume of the liquid. If this does not contain sufficient hydrochloric acid, and if the proportion of sulphuric acid is insufficient, yellow mercury subsulphate may be precipitated, which is avoided by the addition of sulphuric acid. The lead sulphate requires washing with weak alcohol acidulated with sulphuric acid.

Separation of Lead from Silver.

This is, perhaps, the most appropriate place to describe the valuable improvements which the late Mr. D. Forbes made in the separation of silver and lead before the blowpipe. This assay process is in all cases based upon the reduction to a metallic state of all the silver contained in the compound in question along with more or less metallic lead, which latter metal, when not already present in sufficient quantity in the substance itself under examination, is added in the state of granulated lead to the assay previous to its reduction. The globule of silver-lead thus obtained is soft and free from such elements as would interfere with its treatment upon the cupel, and may then be at once cupelled before the blowpipe until the pure silver alone remains upon the bone-ash surface of the cupel; but if not, it is previously submitted to a scorifying or oxidating treatment upon charcoal until all such substances are either slagged off or volatilised, and the resulting silver-lead globule cupelled as before.

As, therefore, the final operation in all silver assays is invariably that of cupelling the silver-lead alloy obtained from the previous reduction of the substance, effected by methods differing according to the nature of the argentiferous ore or compound under examination, it is here considered advisable to introduce the description of the silver assay by an explanation of this process.

In the ordinary process of cupellation in the muffle, bone-ash or other cupels are employed, of a size large enough to absorb the whole of the litharge produced from the oxidation of the lead in the assay.

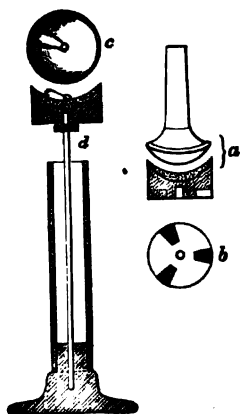
This, however, should not be the case when using the blowpipe; for, as the heating powers of that instrument are limited, it is found in practice much better to accomplish this result by two distinct operations—the first being a concentration of the silver-lead, in which the

greater part of the lead is converted by oxidation into litharge, remaining upon, but not, or only very slightly, absorbed by the bone-ash cupel; the second consisting in cupelling the small concentrated metallic bead so obtained upon a fresh cupel until the remaining lead is totally absorbed by the cupel and the silver left behind in a pure state. By this means a much larger weight of the silver-lead alloy can be submitted to assay, and, for reasons hereafter to be explained, much more exact results are obtained than would be the case when the cupellation is conducted at one operation in the ordinary manner.

The apparatus used by the late Mr. Forbes for these operations are shown to a scale of one-half their real size in the woodcut (Fig. 8, *a* to *d*).

In Fig. 8, *a*, is represented in section a small cylindrical mould of iron, 0.7 of an inch in diameter and about 0.4 high, in which is turned a cup-shaped, nearly hemispherical depression, 0.2 of an inch deep in centre, the inner surface of which is left rough, or marked with minute ridges and furrows for the purpose of enabling it to retain more firmly the bone-ash lining, which is stamped into it by means of the polished bolt also shown in the figure. This mould rests upon the stand, *d*, having for this purpose a small central socket in its base, into which the central pivot of the stand enters. The socket is seen in the

FIG. 8.



ground-plan, *b*, of the base of the mould, which shows likewise three small grooves or slots made in same to enable a steady hold to be taken of it, when hot, by the forceps. The stand itself is composed of a small turned ivory or wood base, fixed into a short piece of strong glass tubing, which, from its non-conducting powers, serves as an excellent handle. In the centre of the base a slight iron rod rising above the level of the glass outer tube serves as a support for the cupel mould, into the socket in the base of which it enters.

Bone-ash is best prepared by burning bones which have been previously boiled several times, so as to extract all animal matter. The best bone-ash is made from the core-bone of the horns of cattle well boiled out and burned. The ash from this is more uniform than from the other bones, which have in general a very compact enamel-like exterior surface, whilst the interior is of a much softer nature.

Concentration of the Silver-Lead.—A cupel is prepared by filling the above-described cupel mould with bone-ash powder not finer than will pass through a sieve containing from 40 to 50 holes in the linear inch; it should be well dried and kept in an airtight bottle, and when used, the whole must be pressed down with the bolt,

using a few taps of the hammer. It is then heated strongly in the oxidating blowpipe flame, in order to drive off any hygroscopic moisture. The bone-ash surface of the cupel, after heating, should be smooth, and present no cracks; if the reverse, these may be removed by using the bolt again and re-heating.¹ The silver-lead, beaten on the anvil into the form of a cube, is placed gently upon the surface of the bone-ash, and, directing a pretty strong oxidating flame on to its surface, it is fused, and quickly attains a bright metallic appearance, and commences to oxidise with a rapid rotatory movement. (Occasionally, when the assay is large, and much copper or nickel present, the globule may, under this operation, cover itself with a crust of lead oxide, or solidify; in such cases direct the blue point of a strong flame steadily on to one spot on the surface of the lead-globule until it commences oxidating and rotating. In some cases, where much nickel is present, an infusible scale, impeding or even preventing this action, may form, but will disappear on adding more lead—say from 8 to 6 grains, according to the thickness of this scale or crust.) When this occurs the cupel is slightly inclined from the lamp, a fine blue point is obtained by placing the blowpipe nozzle deeper into the lamp, and the flame is directed at about an angle of 30° on to the globule—not, however, so near as to touch it with the blue point, but only with the outer flame, so moderating it as to keep the assay at a gentle red heat, and not allowing the rotation to become too violent.

This oxidizing fusion should be carried on at the lowest temperature sufficient to keep up the rotatory movement, and to prevent a crust of litharge accumulating upon the surface of the globule, but still sufficiently high to hinder the metallic globule from solidifying. Should this, however, happen, a stronger flame must be employed for a moment until the metal is again in rotation; such interruptions should, however, be avoided. The proper temperature can only be learned by practice, a too high temperature is still more injurious, causing the lead to volatilise, and, if rich in silver, carry some of that metal mechanically along with it. The litharge, also, instead of remaining on the cupel would be absorbed by the bone-ash, and as the surface of the metallic globule is covered by a too thin coating of fused litharge, some silver may be absorbed along with the litharge. In this operation, in order to avoid loss of silver, the fused globule should be always kept in contact with the melted litharge.

By the above treatment the air has free access to the assay, and the oxidation of the lead and associated foreign metals goes on rapidly. The surface of the melted globule, when poor in silver, shows a brilliant play of iridescent colours, which does not take place when very rich in silver. The litharge is driven to the edge of the globule,

¹ These precautions are very important, as the slightest trace of moisture in the substance of the bone-ash would inevitably cause a spitting of the metal during the operation.

heaping itself up and solidifying behind and around it. When the globule becomes so hemmed in by the litharge as to present too small a surface for oxidation, the cupel is moved so as to be more horizontal (having been previously kept in an inclined position), thus causing the lead-globule to slide by its own weight on one side and expose a fresh surface to the oxidising action. When the lead is pure, the litharge formed has a reddish-yellow colour, but, if copper is present, is nearly black.

In concentrating silver-lead, it must be remembered that an alloy of lead and silver, if in the proportion of about 86 per cent. silver along with 14 per cent. lead, when cooled slowly in the litharge behaves in a manner analogous to the spitting of pure silver, throwing out a whitish-grey pulverulent excrescence rich in silver. For this reason, therefore, the concentration above described should be stopped when the globule is supposed to contain about 6 parts silver along with 1 part in weight of lead. In case, however, this limit should have been exceeded, it is advisable at once to push the concentration still further until the silver globule contains but very little lead. In practice, with poor ores, it is usual to concentrate the lead until the globule is reduced to the size of a small mustard seed, or in rich ores to some two or three times that size. Upon arriving at this point, the cupel is withdrawn very gradually from the flame, so that the cooling shall take place as slowly as possible until the globule has solidified in its envelope of litharge. If cooled too quickly, the litharge, contracting suddenly, would throw out the globule, or even cause it to spirt; in such case it should be touched by the point of the blue flame so as to fuse it to a round globule, which is cooled slowly as before described. The globule is now reserved for the next operation, for which purpose it is, when quite cold, extracted from the litharge surrounding it.

Cupellation.—The bone-ash required for this process should be of the best quality and in the most impalpable powder, prepared by elutriating finely-ground bone-ash and drying the product before use.

The cupel, still hot from the last operation, is placed upon the anvil, and the crust of litharge, with its enclosed metallic bead, gently removed, leaving the hot coarse bone-ash beneath it in the mould; upon this a small quantity of the elutriated bone-ash is placed, so as to fill up the cavity, and the whole whilst hot stamped down by the bolt, previously slightly warmed, with a few taps of the hammer. The cupel thus formed is heated strongly in the oxidating flame, which should leave the surface perfectly smooth, and free from any fissures or scales; if such appear, the bolt must again be used, and the cupel re-heated. In this process it is very important that the cupel should possess as smooth a surface as possible, whilst at the same time the substance of the cupel beneath should not be too compact, so as thereby to permit the litharge to filter through and be readily absorbed, leaving the silver bead upon the smooth upper surface.

The bead of silver-lead obtained from the last operation is taken out of the litharge in which it is embedded, and, after removing any trace of adherent bone-ash or litharge, is slightly flattened to prevent its rolling about upon the surface of the cupel.

It is now put into the cupel prepared as before described, placing it on the side farthest from the lamp and a little above the centre of the cupel, which is now inclined slightly towards the lamp, and is heated by the oxidating flame directed downwards upon it, thus causing the globule when fused and oxidating to move of itself into the centre of the cupel. The cupel is now brought into a horizontal position, and the flame, directed on to it at an angle of about 45 degrees, is made to play upon the bone-ash surface immediately surrounding the globule, without, however, touching it; so as to keep this part of the cupel at a red heat sufficiently strong to insure the globule being in constant oxidising fusion, and at the same time to cause the perfect absorption of the litharge, and prevent any scales of litharge forming upon the surface of the cupel under the globule, which would impede the oxidation, as well as prevent the silver bead being easily detached at the conclusion of the operation. Should the heat at any time be too low and the globule solidify, it must be touched for an instant with the point of the flame and proceeded with as before. Should (in consequence of the bone-ash not having been sufficiently heated to absorb the litharge perfectly) a little litharge adhere pertinaciously to the globule, or a particle of the bone-ash cupel attach itself, the cupel should be slightly inclined, so as to allow the globule to move by its own weight on to another and clean part of the cupel, leaving the litharge or bone-ash behind it; but, if not sufficiently heavy to do so, a small piece of pure lead may be fused to it in order to increase its weight, and so allow of the same proceeding being adopted.

By slightly inclining the cupel stand, and moving it so as to present in turn all parts of the surface surrounding the globule to the action of the flame, the cupellation proceeds rapidly. If, however, the assay contains very little silver, it will be found necessary to move the globule from one spot to another on the cupel, in order to present a fresh surface for absorbing the litharge formed; this is done by simply inclining the cupel stand, remembering that the bone-ash surrounding the globule must always be kept at a red heat, without ever touching the globule itself by the flame.

In assays rich in silver a play of iridescent colours appears some seconds before the 'brightening,' which disappears the moment the silver becomes pure; as soon as this is observed the cupel should be moved in a circular manner, so that the globule is nearly touched all round by the point of the blue flame, and this is continued until the surface of the melted silver is seen to be quite free from any litharge, upon which it is very gradually withdrawn from the flame, so as to cool the assay by degrees very slowly, in order to prevent 'spitting.'

When the silver-lead is very poor, this play of colours is not apparent, and as soon as the rotatory movement of the globule ceases, the heat must be increased for an instant in order to remove the last thin but pertinacious film or scale of litharge, and subsequently the assay is cooled gradually; when cold it should, whilst still upon the cupel, be examined by a lens to see whether the bead possesses a pure silver colour, as if not it must be re-heated.

Frequently, when the 'brightening' takes place, the silver globule is found to spread out, and, after cooling, although of a white colour, is found to appear somewhat less spherical or more flattened in shape than a corresponding globule of pure silver would be. This arises from the presence of copper still remaining in the silver, and in such cases a small piece of pure lead (about from 0.5 grain to 1.5 grain in weight, according to size of assay) should be fused on the cupel along with the silver, and the cupellation of the whole conducted as before on another part of the cupel, when the silver globule will be obtained pure and nearly spherical in shape. Sometimes the silver globule in 'brightening' may still remain covered with a thin film of litharge, although otherwise pure; this arises from too little heat having been employed in the last stage of the operation, and consequently the bead should be re-heated in a strong oxidating flame until this litharge is absorbed, and the globule, after slow cooling, appears pure.

If the instructions here given be strictly attended to, it will be found, after some practice, that very accurate results may be obtained in the blowpipe assay for silver, and that no difficulty will be found in detecting the presence and estimating the amount of silver present, even when in as small a quantity as 0.5 ounce to the ton. When substances containing very little silver, or less than that amount, are examined, several assays should be made, and the silver-lead obtained concentrated separately, after which the various globules should be united and cupelled together in one operation.

It is hardly necessary to remark that the lead employed in assaying should be free from silver, or, if not, its actual contents in silver should be estimated, and subtracted from the amount found in the assay.

Assay lead containing less than 0.25 ounce to the ton of lead can readily be obtained, or can be made by precipitating a solution of acetate of lead by metallic zinc, rejecting the first portion of lead thrown down. In all cases the lead should be fused and granulated finely—the granulated lead for use in these assays being previously passed through a sieve containing 40 holes to the linear inch. It is also useful to have some lead in the form of wire, as being very convenient for adding in small portions to assays when on the cupel.

Estimation of the Weight of the Silver Globule obtained on Cupellation.—As the amount of lead which can, by the method above described, be conveniently cupelled before the blowpipe is

necessarily limited, the silver globule which remains upon the bone-ash surface of the cupel at the end of the operation is, when substances poor in silver have been examined, frequently so very minute that its weight could not be estimated with correctness by the most delicate balances in general use.

Globules of silver of far less weight than $\frac{1}{1000}$ of a grain are distinctly visible to the naked eye—a circumstance which induced Harkort to invent a volumetrical scale based upon the measurement of the diameters of the globules, which scale in practice has been found of very great utility in the blowpipe assay of silver.

The scale for this purpose consists of a small strip of highly polished ivory about $6\frac{1}{2}$ inches long, $\frac{3}{8}$ inch broad, and $\frac{1}{8}$ inch in thickness, on which are drawn, by an extremely fine point, two very fine and distinct lines emanating from the lower or zero point, and diverging upwards until, at the distance of exactly 6 English standard inches, they are precisely $\frac{1}{100}$ part of an inch apart. This distance (6 inches) is divided into 100 equal parts by cross lines numbered in accordance from zero upwards. It is now evident, if a small globule of silver be placed in the space between these two lines, using a magnifying-glass to assist the eye in moving it up or down until the diameter of the globule is exactly contained within the lines themselves, that we have at once a means of estimating the diameter of the globule itself, and therefrom are enabled to calculate its weight.

As the silver globules which cool upon the surface of the bone-ash cupel are not true spheres, but are considerably flattened on the lower surface where they touch and rest upon the cupel, it follows that the weight of globules corresponding in diameter to the extent of divergence at the different degrees of the scale cannot be calculated directly from their diameters as spheres, but require to have their actual weight experimentally estimated in the same manner as employed by Plattner.

The table here appended is an abstract of one calculated by Mr. Forbes, and in one column shows the diameter in English inches corresponding to each number or degree of the scale itself, and in the next column the respective weights of the flattened spheres which correspond to each degree or diameter. For ordinary purposes the intermediate weights may safely be obtained by interpolation, but if great accuracy is needed the full table should be consulted. It is given in the *Chemical News* for June 7, 1867, vol. xv. p. 281.

These weights are calculated from the following data, found as the average result of several very careful and closely approximating assays, which showed that globules of silver exactly corresponding to No. 95 on this scale, or 0.098 inch in diameter, possessed a weight of 0.0475573 grain. From this the respective weights of all the other numbers or degrees on this scale were calculated, on the principle that solids were to one another in the ratio of the cubes of their diameters. This mode of calculation is not, however, absolutely

correct in principle, for the amount of flattening of the under surface of the globule diminishes in reality with the decreasing volume of the globule. In actual practice, however, this difference may be assumed to be so small that it may be neglected without injury to the correctness of the results.

The smaller the diameter of the globule, the less will be the difference or variation in weight in descending the degrees of this scale, since the globules themselves vary in weight with the cubes of their diameters; for this reason, also, all such globules as come within the scope of the balance employed should be weighed in preference to being measured, and this scale should be regarded as more specially applicable to the smaller globules beyond the reach of the balance.

No. on scale	Greatest diameter in inches	Weight of globule in grains
1	0.0004	0.00000005
2	0.0008	0.00000044
3	0.0012	0.00000149
4	0.0016	0.00000355
5	0.0020	0.0000069
6	0.0024	0.0000119
7	0.0028	0.0000190
8	0.0032	0.0000284
9	0.0036	0.0000403
10	0.0040	0.0000554
15	0.0060	0.0001872
20	0.0080	0.0004437
25	0.0100	0.0008667
30	0.0120	0.0014976
40	0.0160	0.0035550
50	0.0200	0.0069335
60	0.0240	0.0119815
70	0.0280	0.0190256
80	0.0320	0.0284000
90	0.0360	0.0404368
100	0.0400	0.0554688

Cupellation Loss.—This term is applied to indicate a minute loss of silver, unavoidably sustained in the process of cupellation, which arises from a small portion of that metal being mechanically carried along with the litharge into the body of the cupel. The amount of this loss increases with the quantity of lead present in the assay (whether contained originally in the assay or added subsequently for the purpose of slagging off the copper, &c.); it is relatively greater as the silver globule is larger, but represents a larger percentage of the silver actually contained in the assay in proportion as the silver globule obtained diminishes in size. It has, however, been experimentally proved that in assays of like richness in silver, this loss remains constant when the same temperature has been employed and similar weights of lead have been oxidised in the operation.

In the blowpipe assay this loss is not confined to the ultimate operation of cupellation, but occurs, though in a less degree, in the concentration of the silver-lead, and in the previous scorification of the assay, when such operation precedes the concentration. The total loss in the blowpipe assay is found, however, to be less than in the ordinary muffle assay, since, in the latter case, the whole of the oxidised lead is directly absorbed by the cupel.

In mercantile assays of ore it is not customary to pay attention to the cupellation loss, and the results are usually stated in the weight of silver actually obtained. Where, however, great accuracy is required, especially when the substances are very rich in silver, the cupellation loss is added to the weight of the silver globule obtained in order to arrive at the true percentage.

The amount to be added for this purpose is shown in the annexed table, which is slightly modified from Plattner's:—

Actual percentage of silver found by assay	Cupellation loss, or percentage of silver to be added to the actual percentage found by assay in order to show the true percentage of silver contained in same, the entire amount of lead in or added to the assay being the following multiples of the original weight of assay:—									
	1	2	3	4	5	6	8	11	13	16
99·75 } 99·50 }	0·25	0·32	0·39	0·45	0·50	—	—	—	—	—
90 ...	0·22	0·29	0·36	0·42	0·47	0·69	0·83	—	—	—
80 ...	0·20	0·26	0·33	0·39	0·44	0·64	0·75	—	—	—
70 ...	0·18	0·23	0·29	0·35	0·40	0·58	0·68	0·82	—	—
60 ...	0·16	0·20	0·26	0·30	0·36	0·52	0·61	0·74	—	—
50 ...	0·14	0·17	0·23	0·26	0·32	0·46	0·54	0·65	—	—
40 ...	0·12	0·15	0·20	0·22	0·27	0·39	0·46	0·55	0·62	—
35 ...	0·11	0·13	0·18	0·18	0·25	0·36	0·42	0·50	0·57	—
30 ...	0·10	0·12	0·16	0·16	0·22	0·32	0·38	0·45	0·51	—
25 ...	0·09	0·10	0·14	0·14	0·20	0·29	0·34	0·40	0·45	—
20 ...	0·08	0·09	0·12	0·12	0·17	0·25	0·29	0·35	0·39	0·45
15 ...	0·07	0·08	0·10	0·11	0·15	0·20	0·23	0·28	0·32	0·37
12 ...	0·06	0·07	0·09	0·10	0·13	0·17	0·19	0·23	0·26	0·32
10 ...	0·05	0·06	0·08	0·09	0·11	0·15	0·17	0·20	0·23	0·27
9 ...	0·04	0·05	0·07	0·08	0·10	0·14	0·16	0·18	0·21	0·25
8 ...	0·03	0·04	0·06	0·07	0·09	0·13	0·15	0·16	0·18	0·22
7 ...	0·02	0·03	0·05	0·06	0·08	0·12	0·13	0·14	0·16	0·20
6 ...	0·01	0·02	0·04	0·05	0·07	0·10	0·11	0·12	0·14	0·17
5 ...	—	0·01	0·03	0·04	0·06	0·09	0·10	0·11	0·12	0·14
4 ...	—	—	0·02	0·03	0·05	0·07	0·08	0·09	0·10	0·11
3 ...	—	—	0·01	0·02	0·04	0·05	0·06	0·07	0·08	0·09
2 ...	—	—	—	0·01	0·03	0·04	0·04	0·05	0·06	0·07
1 ...	—	—	—	—	0·01	0·03	0·03	0·04	0·04	0·05

The use of the above table is best explained by an example, as the following:—An assay to which there had been added, in all, five times its weight of assay lead, gave a globule of silver equivalent to 6 per cent. Upon referring to the table, it will be seen that the cupellation loss for this would be 0·07; consequently, the true percentage of silver contained in the assay would be 6·07. This table is only extended

to whole numbers, but fractional parts can easily be calculated from the same.

When the globules of silver are so minute that they cannot be weighed, but must be measured upon the scale, the cupellation loss should not be added, since, as a rule, it would be less than the difference which might arise from errors of observation likely to occur when measuring their diameters upon the scale.

In the case of beginners, it will be found that the cupellation is usually carried on at too high a temperature, and that thereby a greater loss is occasioned than would be accounted for by the above table. After some trials, the necessary experience will be acquired in keeping up the proper temperature at which this operation should be effected.

It is not necessary to consider in detail the processes requisite for extracting the silver contents (in combination with lead) from the various silver ores and other argentiferous compounds which are met with in nature or produced in the arts, as this would be to exceed the limits of analysis proper. The following classification of substances will, however, be found convenient:—

I. METALLIC ALLOYS.

A. Capable of direct cupellation.

- a. Consisting chiefly of lead or bismuth: silver, lead, and argentiferous bismuth, native bismuthic silver.
- b. Consisting chiefly of silver: native silver, bar silver, test silver, precipitated silver, retorted silver amalgam, standard silver, alloys of silver with gold and copper.
- c. Consisting chiefly of copper: native copper, copper ingot, sheet or wire, cement copper, copper coins, copper-nickel alloys.

B. Incapable of direct cupellation.

- a. Containing much copper or nickel, with more or less sulphur, arsenic, zinc, &c.: unrefined or black copper, brass, german silver.
- b. Containing tin: argentiferous tin, bronze, bell-metal, gun-metal, bronze coinage.
- c. Containing antimony, tellurium, or zinc.
- d. Containing mercury: amalgams.
- e. Containing much iron: argentiferous steel, bears from smelting furnaces.

II. MINERALISED COMPOUNDS.

- a. Silver and other ores, furnace products, sweeps, and products of the arts containing sulphides, arsenides, and other compounds of the metals in combination with more or less earthy matters.

- b.* Argentiferous molybdenum sulphide.
- c.* Substances nearly free from sulphides or arsenides, but containing chlorine, iodine, or bromine.
- d.* Argentiferous litharge and other easily reducible oxides.

To give information on the treatment of these substances belongs to the subject of assaying, a branch of analysis of which we have not space now to treat. The reader who wishes to follow out the subject is referred to 'A Manual of Practical Assaying,'¹ edited by the author of this work.

Separation of Lead from Zinc.

The best method of separating small quantities of lead from zinc, as in the analysis of commercial spelter, is to add potassium bichromate and acetic acid to the neutral solution of the metals. A trace of lead causes the formation of a yellow precipitate. For further particulars, see page 846.

For the separation of a mixture of lead, zinc, and silver, Mr. F. Maxwell Lyte treats the ore, ground and calcined, with dilute hydrochloric acid in troughs of resinous wood, into which steam is blown to raise the temperature. The zinc, lead, and silver are thus converted into chlorides, the argentic and a part of the plumbic chloride remaining mixed with the gangue. The liquid is then run off, and allowed to cool, when nearly the whole of the plumbic chloride is deposited. The clear mother-liquid, containing zinc chloride and excess of hydrochloric acid, is syphoned back into the first tank, where it takes up a fresh quantity of lead and silver chlorides, the gangue being thus exhausted after three successive decantations. To the entire solution now existing in the second tank scrap-zinc is added, when all the lead and silver is deposited as a metallic sponge. (It must be remembered that silver chloride is soluble in concentrated solutions of lead chloride.) From the residual liquor the zinc is precipitated as oxide by the addition of milk of lime.

Separation of Lead from Barium when in the Form of Sulphates.

Sodium thiosulphate dissolves lead sulphate, and may be used to separate this salt from the barium sulphate. To effect this separation a concentrated solution of the thiosulphate must be added to the mixture of the two salts, and the whole gently warmed, taking care that the temperature does not exceed 68° C.; at a higher temperature lead sulphite is formed, which is insoluble in the thiosulphate.

The residue of barium sulphate is carefully washed and weighed; to control the results the lead in the thiosulphate may be estimated.

¹ London: Longmans and Co. 1881.

White Lead.

Commercial white lead is frequently adulterated with barium sulphate and calcium carbonate. The presence of barium sulphate may be tolerated when its proportion does not exceed 5 per cent.

M. Gaston Tissandier proposes the following method of analysis:—Weigh 1 gramme of white lead, and calcine it in a small porcelain capsule; treat the residue, while hot, with pure nitric acid diluted with water; this dissolves the lead oxide, while the barium sulphate remains insoluble.

Now filter, and precipitate the filtered liquid with sulphuretted hydrogen; a formation of lead sulphate will then ensue, and this must be dried at 100° C. and weighed. The liquid, separated from lead sulphide, is treated with ammonia and ammonium sulphhydrate, which will betray the presence of zinc oxide, which sometimes occurs in white lead, by precipitating it as zinc sulphide. Filter this latter, and evaporate the filtered liquid to dryness, previously adding hydrochloric acid; take up the residue with water and hydrochloric acid, and add ammonia and ammonium oxalate, which will precipitate the lime as insoluble calcium oxalate.

The lead sulphide is converted by calcination into carbonate; the zinc sulphide is dissolved in hydrochloric acid after calcination, and precipitated as zinc carbonate. The zinc carbonate is collected on a filter, washed with boiling water, dried, calcined, and weighed; the calcination transforms it into zinc oxide, which is thus extracted directly from the specimen of colour under examination.

To ascertain whether the white substance which was insoluble in the acid liquid used in the first experiment be really barium sulphate, proceed as follows:—Mix it thoroughly with dry, pure, finely powdered sodium carbonate; heat it to redness in a platinum crucible, until the fluid mass no longer effervesces, let it cool, and boil it in warm water, which dissolves the sodium sulphate formed, without acting upon the barium carbonate which is formed during the reaction. The aqueous solution should be precipitated by barium chloride, which determines the formation of insoluble barium sulphate; the insoluble substance remaining on the filter is treated with pure hydrochloric acid diluted with water, and should yield a precipitate of barium sulphate on the addition of a drop of sulphuric acid.

Analysis of Minium or Red Lead.

Thomas P. Blunt proposes the following process:—

1. **Iron.**—100 grains of minium are dusted gradually into $\frac{1}{2}$ -ounce of pure redistilled hydrochloric acid contained in a beaker; torrents of chlorine are given off, and the consequent agitation of the liquid prevents caking, which invariably occurs when the acid is poured over the weighed sample, and is very troublesome, as it prevents the

interior of the lumps from being properly acted upon by the acid. The beaker and its contents are now transferred to the water-bath, and evaporation is carried almost to dryness; the residue is then diluted with some quantity of water and the whole allowed to cool; the clear liquid is now decanted off as closely as possible from the lead chloride which has precipitated, and the latter is washed with a small quantity of cold water, the rinsings being added to the bulk of the liquid, which need not be absolutely clear. Sulphuric acid is then added, and the precipitation, decantation, and slight washing repeated.

The liquid, which is now almost free from lead (though still retaining traces apparently in the form of a per-salt not entirely decomposable by sulphuric acid) is in a fit state for the estimation of iron and copper. Ammonia in considerable excess is added, and the precipitate is collected on a filter and washed. It is yellowish-white in colour, and contains all the iron and some lead. After thorough washing the filter is pierced, the precipitate washed into a small flask as completely as possible, and the filter rinsed several times with dilute sulphuric acid, which is allowed to run into the flask; the whole is then warmed, upon which the iron oxide is dissolved, and the traces of lead-salts converted into sulphate, which does not interfere with the succeeding operation, though it is reduced to the metallic state. The liquid is now heated for some time with a few fragments of perfectly pure zinc, filtered, and titrated with very weak permanganate solution, which may be conveniently delivered from a pipette divided into grains. The permanganate solution should be of such strength that at least 1000 grain measures are required to peroxidise 1 grain metallic iron.

2. Copper.—The ammoniacal filtrate from the iron oxide is neutralised with acetic acid and divided into 2 equal portions; to one of them is added a small measured quantity (about 8 grains) of ordinary potassium ferrocyanide solution; a red colour will be produced more or less deep according to the quantity of copper present; the liquid is filtered *immediately*¹ through close paper, and if the red colour is not entirely removed it is passed a second time through the same filter. The clear and very faintly yellow solution is then transferred to one of two twin beakers, the other containing the second portion of solution from which the copper has not been removed. A measured quantity (about 20 grains) of acetic acid is now added to each, and 8 grain measures of ferrocyanide solution to that which has not yet received any; the beakers are placed on a white surface, and the colour produced by the copper in the second beaker is matched in the first by the gradual addition, with stirring, of a standard solution of copper sulphate from a graduated pipette, about a minute being allowed

¹ If the filtration be delayed, a yellow colour is produced, which interferes materially with the subsequent operation; it appears to be due to the oxidation of the ferro- to ferri-cyanide.

between each addition for the full development of the tint. The copper solution is made by dissolving 39.3 grains of pure crystallised copper sulphate (free from efflorescence) in 10,000 grains of distilled water, which gives 1 part of metallic copper in 1000 measured grains. The number of grain measures required multiplied by 2 and transferred to the third decimal place, gives the percentage of metallic copper; thus, —to take an actual case— $8\frac{1}{2}$ grain measures of the solution were required to match the tint given by the copper in a minium treated as above; therefore the sample contained 0.007 per cent. of copper.

It is absolutely necessary to use a comparison liquid prepared in the manner described, and corresponding exactly to the solution to be tested, except that it contains no copper, since it has been proved by careful experiment that the quantity of ammoniacal salts present has a material effect upon the tint produced.

3. Metallic Lead.—This impurity is generally found in the form of minute beads distributed throughout the sample; it is best detected and estimated by dissolving the lead oxides in glacial acetic acid in the following manner:—One ounce of acetic acid of the kind commercially described as ‘glacial at 82°’ is placed in a beaker, and 20 grains of the minium—which must, of course, be in fine powder—is dusted into it; the beaker is placed in warm water (about 100° F.), and the contents frequently stirred; in the course of from a quarter to half an hour the whole of the lead oxides present will be dissolved, metallic lead remaining behind, together with any foreign matter, such as bole, which may have been added as an adulterant. The solution may be decanted off, and the residue washed, first with glacial acid and then with water, dried, and weighed.

It has been found that minute fragments of bright metallic lead are not appreciably acted upon by the acetic solution of minium, in spite of its well-known powerfully oxidising properties, but are merely superficially tarnished without entirely losing their lustre.

4. Silver.—200 grains of minium are treated with a mixture of $\frac{1}{2}$ -ounce of nitric acid, sp. gr. 1.42, entirely free from chlorine, and $1\frac{1}{4}$ ounce distilled water also free from chlorine, and giving no turbidity with silver nitrate; the mixture becomes hot. It is stirred at intervals during 2 hours, and is then diluted with pure distilled water to about 4 ounces and filtered, the residue being washed once with a small quantity of distilled water. The filtrate, which should measure from $4\frac{1}{2}$ to 5 ounces, is then divided into 2 equal parts. The rest of the process is similar in principle to that employed for copper, but here turbidity, not colour, forms the basis of comparison. The two halves of the liquid having been placed in two similar beakers, one is set aside and covered with a watch-glass, to the other is added 1 drop of strong hydrochloric acid; a precipitate will appear which redissolves on stirring, leaving only a faint turbidity due to the silver. Allow to stand for a short time and filter, washing once with a few drops of

distilled water; return the filtrate and washings to the beaker, and place the latter beside that which has been set aside. Both beakers should be placed *in front* of a black surface of cloth or dull silk, to facilitate the estimation of the turbidity. Add now 1 drop of strong hydrochloric acid to the beaker from which the silver has not been removed, stir, and note the turbidity produced, which is to be matched in the other beaker by stirring in measured quantities—about 1 grain at a time—of a dilute solution of silver nitrate, prepared by dissolving 15·7 grains of the crystals in 10,000 grains of pure distilled water. The solution contains 0·001 grain metallic silver in every measured grain, and consequently the number of grain measures added to produce the required turbidity gives the percentage of silver at the third decimal place. An interval of about half a minute should be allowed between each addition, and both solutions should be frequently stirred during the operation. The use of the ‘comparison liquid’ is rendered necessary by the fact that the dissolved lead salts diminish the apparent turbidity produced by the silver chloride. The phenomenon is not easy of explanation, as it is independent of any solvent action, and takes place equally in a solution which has been saturated with silver chloride by a previous precipitation.

Separation of Gallium from Lead.

This may be effected by six methods:—

1. The hydrochloric solution, slightly acid, is diluted with a little water and submitted to ebullition in presence of an excess of cupric hydrate. The gallium precipitated retains but a feeble trace of lead, which is entirely eliminated by a second similar treatment. The reagents employed must be free from sulphuric acid or sulphates, or otherwise lead sulphate will remain upon the filter along with gallium oxide. The copper and the lead are then separated by known methods. The present process is very exact, and is suitable for removing from gallium sulphate the small quantity of lead which remains in solution after precipitation with sulphuric acid.

2. The separation of lead is also effected accurately if the hydrochloric or sulphuric solution is boiled first with metallic copper and then with cuprous oxide. This method is specially applicable when iron has to be separated at the same time as lead. The first cuprous precipitate contains scarcely a feeble trace of lead, so that two operations are sufficient. If we operate upon a chloride the presence of sulphuric acid must be carefully avoided.

3. The solution—sulphuric, hydrochloric, or nitric—perceptibly though moderately acid, is saturated with hydrogen sulphide, filtered, and evaporated almost to dryness, in order to expel the bulk of the free acid. It is then diluted with water, and again saturated with hydrogen sulphide. After two or three similar treatments, the gallium salt no longer contains an appreciable trace of lead. The lead sulphides

generally retain a trace of gallium, which may be removed by attacking them with concentrated hydrochloric acid, adding alcohol, filtering, evaporating to expel the alcohol and the bulk of the acid, diluting with water, and finally saturating with sulphuretted hydrogen.

4. In a liquid containing from one-fourth to one-third of its volume of strong hydrochloric acid, potassium ferrocyanide precipitates gallium ferrocyanide, generally free from lead. In case of need the gallium salt may be taken up in a small quantity of potash and reprecipitated by adding much hydrochloric acid and a little potassium ferrocyanide.

5. It is often convenient to begin by precipitating almost all the lead by means of sulphuric acid. The liquid is then mixed with double its volume of alcohol at 90°. If properly washed with alcohol, acidulated with sulphuric acid, the lead sulphate does not contain appreciable traces of gallium. To detect such traces the lead sulphate is suspended in water, acidulated with hydrochloric acid, and treated with a prolonged current of hydrogen sulphide. The filtrate is boiled in order to expel hydrogen sulphide, and treated in heat with cupric hydrate, which precipitates the traces of gallium oxide. The alcoholic solutions derived from the sulphuric precipitation of lead are freed from alcohol by boiling; the gallium oxide is then separated by means of cupric hydrate.

6. The solution (nitric or other) is mixed with twice its volume of alcohol at 99 per cent., and a small excess of hydrochloric acid. The lead chloride when washed with acidulated alcohol does not retain gallium. The alcoholic liquids are concentrated to a small volume, freed from nitric acid, and treated either with hydrogen sulphide (process No. 8), or with cupric hydrate, or metallic copper and cuprous oxide (processes Nos. 1 and 2).

Valuation of Commercial Lead Peroxide.

H. Fleck recommends the introduction of a weighed quantity (0.5 gramme) into a standard solution of ammonium ferrous sulphate, adding not more hydrochloric acid than is required for the decomposition of the lead peroxide. After heating, the liquid is diluted with boiled water cooled down to the temperature of the room, and titrated with permanganate.

Another process is to decompose a weighed quantity of the sample with sufficient hydrochloric acid in a small flask fitted with a gas delivery-tube. The chlorine gas given off is passed into a solution of potassium iodide, and the iodine liberated is estimated in the known manner with sodium thiosulphate. The moisture of the samples is found by drying at 110°.

THALLIUM.

Detection of Thallium in Minerals.

The optical process of detecting thallium in a mineral is very simple. A few grains of the ore are crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, and examining the light by means of a spectro-scope, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eyepiece of the spectro-scope to protect the eye from the glare of the sodium line, thallium may be detected in $\frac{1}{2}$ grain of mineral, when it is present only in the proportion of 1 to 500,000. The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present. Before deciding whether a deposit or mineral contains sufficient of the metal to be worth extracting, it is necessary to make a rough analysis in the wet way by methods which will be subsequently described.

Thallium is a very widely distributed constituent of iron and copper pyrites. Upon examining a large collection of pyrites from different parts of the world, it was found present in more than one-eighth. It is not confined to any particular locality. Amongst those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the $\frac{1}{100000}$ to the $\frac{1}{4000}$ of the bulk of the ore), may be mentioned iron pyrites from Theux, near Spa in Belgium, from Namur, Philipville, Alais, the South of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, cadmium sulphide, metallic cadmium, and cake sulphur from Nouvelle Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

Thallium is likewise frequently present in copper and commercial salts of this metal. In Spain a very impure copper is prepared in the following way:—Copper pyrites is allowed to oxidise in the air, and the resulting copper sulphate is washed out; scrap iron is now placed in the liquid, which causes the copper to precipitate in a powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting-point. It is brought over to this country in the form of rectangular cakes, weighing about 20 pounds each, and is called 'cement copper.' The thallium sulphide oxidising to sulphate

along with the copper sulphide is washed out by the water, and precipitated with the copper by the iron. The two metals alloy together.

Thallium is present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald. It has likewise been found in the deliquescent 'Sel-à-Glace' from the mother-liquors of the salt-works at Neuheim. This consists of a mixture of the magnesium, potassium, and sodium chlorides, with relatively considerable quantities of rubidium and caesium chlorides, and sensible traces of thallium chloride. Thallium is also met with in the mother-liquors in the zinc sulphate works at Goslar, in the Harz.

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric acid works.

Preparation of Thallium.

a. From the Flue-Dust of Pyrites-burners.—This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid, the thallium oxidises along with the sulphur, and is driven off by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and volatilises into the leaden chambers; it there meets with aqueous vapours, sulphurous and sulphuric acids, and becomes converted into thallium sulphate. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with the multiplicity of other bodies which constitute 'flue-dust.' Accompanying the thallium have been found mercury, copper, lead, tin, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various. In many specimens it is not present at all, and in very few it amounts to as much as $\frac{1}{4}$ per cent., although in some as much as 8 per cent. of thallium have been found. The following is the best plan for extracting this metal from the dust:—The dust is first heated to very dull redness, so as to allow the excess of sulphuric acid to drive off any hydrochloric acid which may be present, and is then mixed in wooden tubs with an equal weight of boiling water, and well stirred; after this, the mixture is allowed to rest for 24 hours for the undissolved residue to deposit. The liquid is then syphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors, which have been syphoned off from the deposit, are allowed to cool, precipitated

by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure thallium chloride, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of flue-dust treated in this way yielded the author 68 pounds of this rough chloride.

The next step consists in treating the crude chloride in a platinum dish with an equal weight of strong sulphuric acid, and afterwards heating the mixture to expel the whole of the hydrochloric acid. To make sure of this the heat must be continued until the greater part of the excess of sulphuric acid is volatilised. After this the mass of thallium bisulphate is dissolved in about 20 times its weight of water, nearly neutralised with chalk, and then filtered. On the addition of hydrochloric acid to the filtrate nearly pure thallium chloride is thrown down; this is collected on a filter, well washed, and then dried. The crude thallium protochloride obtained by either of the above methods is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused bisulphate is now to be dissolved in an excess of water, partially neutralised with sodium carbonate, and an abundant stream of sulphuretted hydrogen passed through the solution. The precipitate, which may contain tin, arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrosulphuric acid is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron and alumina, which generally appears in this place, is filtered off, and the clear solution evaporated to a small bulk. Thallium sulphate will then separate out on cooling in the form of long, clear prismatic crystals. As ammonium sulphate is much more soluble than thallium sulphate, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallise together.

In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of thallium chloride, it is less troublesome, although not quite so accurate, to proceed as follows:—Boil the thallium chloride in solution of ammonium sulphide for 5 minutes: decomposition takes place readily. Filter and wash with sulphuretted water till no more chlorine can be detected in the filtrate; then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia, &c., as above directed.

In order to obtain the metal when working on small quantities of material, thallium sulphate is dissolved in 20 times its weight of water; the liquid is acidulated with sulphuric acid, and a current of electricity from two or three cells of Grove's batteries is passed through it, platinum terminals being used. The appearance presented when a tolerably

strong solution of thallium is undergoing reduction is very beautiful. If the E.M.F. of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fernlike branches, spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance being more beautiful than with any other metal. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well-defined; considerable difficulty is, however, met with in disengaging them from the electrode and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate strength of current: as soon as bubbles of gas are evolved the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a mass round the platinum terminal, disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash-bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It coheres together readily by pressure, and will be found to retain its metallic lustre perfectly under water.

When considerable quantities of thallium are to be reduced to the metallic state, it is convenient to employ metallic zinc for the purpose. In the course of 24 hours, the author has reduced upwards of a quarter of a hundredweight of metal in the following way:—Plates of pure zinc (which should leave no residue whatever when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallised thallium sulphate, in quantities of about 7 pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and in the course of a few hours the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zinc removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion.

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under potassium cyanide on the small scale, and under coal-gas when working with large quantities. In the former case the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropped one by one into potassium cyanide kept fused in a porcelain crucible. They rapidly melt, forming a brilliant metallic button at the bottom. When cold, the potassium cyanide may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod, and the thallium may either be poured into water and obtained in a granulated form, or cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being appreciably acted upon by the melted thallium.

b. From Iron Pyrites.—The richest pyrites which the author has yet met with comes from Oneux, near Theux; it contains about 1 part of thallium in 4000. Two tons of this ore were worked in the following manner:—

The pyrites, broken up into pieces of the size of a walnut, is distilled in hexagonal cast-iron pipes, closed at one end, and arranged in a reverberatory furnace. Conical sheet-iron tubes are luted on to the open ends, and the retorts are kept at a bright red heat for about 4 hours. At the end of the operation, the receivers are found to contain from 14 pounds to 17 pounds of dark green or grey-coloured sulphur for every 100 pounds of ore used. The whole of the thallium originally in the pyrites will be found in this sulphur, from which it has now to be separated. The sulphur may be dissolved out by means of carbon bisulphide, which leaves the thallium sulphide behind; or it may be extracted by boiling with caustic soda. The former plan occasions less loss of thallium, but owing to the inconvenience of working with large bulks of carbon bisulphide, the soda process is preferable. Twelve pounds of caustic soda, 18 pounds of the thalliferous sulphur, and $1\frac{1}{2}$ gallon of water are boiled together till the sulphur is dissolved; 6 gallons of water are added, and the clear liquid, when cool, is decanted from a voluminous black precipitate, which has been separated from the sulphur. The precipitate is then collected on a calico filter and washed. It contains the greater portion of the thallium in the form of sulphide, together with iron, copper, mercury, zinc, &c. Some thallium, however, remains dissolved in the alkaline liquid, and is lost. The black precipitate is then dissolved in hot dilute sulphuric acid, to which a little nitric acid is added, and the liquid is diluted with water and filtered. Hydrochloric acid and sodium sulphite will now throw down the nearly insoluble white thallium protochloride, which is to be filtered off and washed.

c. From Sulphur or Pyrites in the Wet Way.—The material is dissolved in nitro-hydrochloric acid, until nothing but bright yellow sulphur is left; water is then added, and the filtrate is evaporated with sulphuric acid, until it is nearly dry, and sulphuric vapours are copiously evolved. The residue is dissolved in large excess of hot water, and sodium carbonate is added to alkaline reaction, and then potassium cyanide (free from potassium sulphide). The liquid is then

heated gently for some time, and filtered. The precipitate contains the whole of the lead and bismuth which may be present, as carbonates, whilst the thallium is in solution. A current of sulphuretted hydrogen being now passed through the alkaline liquid precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. The precipitated sulphide is filtered off, washed, and dissolved in dilute sulphuric acid, and the thallium is precipitated by means of hydrochloric acid as chloride, from which the metal is extracted in the way described on page 878.

d. From the Saline Residues of the Salt-works at Neuheim.—Böttger adds a small quantity of platinum bichloride to the strong solution, and boils the precipitate five or six times with 8 times its weight of water. The insoluble residue consists of the platinum-salts of caesium, rubidium, and thallium. Upon boiling these with a weak solution of potash and a little sodium thiosulphate, the solution soon becomes clear, whereupon potassium cyanide and sulphuretted hydrogen are added. This precipitates the thallium as sulphide. The liquid is then to be filtered, the residue washed and dissolved in sulphuric acid, and the metal precipitated by metallic zinc.

e. From Commercial Hydrochloric Acid.—Many samples of yellow hydrochloric acid contain thallium. It may be separated by neutralising with an alkali and adding ammonium sulphide. The black precipitate contains the thallium, together with iron and some other metallic impurities of the acid. It is to be dissolved in sulphuric acid, and the thallium precipitated with hydrochloric acid as protochloride. This is afterwards reduced as already described.

f. From the Mother-Liquors of the Zinc Sulphate Works at Goslar.—Each kilogramme of these liquors is said to yield as much as $\frac{1}{2}$ gramme of thallium chloride. A sheet of zinc is plunged into the liquid, whereby the thallium, copper, and cadmium are precipitated. The metallic sponge is then removed from the zinc, washed, and treated with cold dilute sulphuric acid, which dissolves the cadmium and thallium with disengagement of hydrogen, whilst the copper is left behind. The filtrate from the copper is then mixed with hydrochloric acid, which precipitates the nearly insoluble thallium chloride. If only a small quantity of thallium is present, potassium iodide may be used as a precipitant, as the thallium iodide is insoluble in water.

Preparation of Chemically pure Thallium.

a. Commercial thallium sulphate is dissolved in water, and the cold solution deluged with sulphuretted hydrogen. It is then filtered, heated to ebullition and poured into boiling dilute hydrochloric acid. The solution is filtered whilst hot and then allowed to cool. The thallium chloride which crystallises out on cooling is washed by decantation until the washings are free from sulphuric acid, and further

purified by recrystallising twice from water. The thallium chloride thus obtained is dried, mixed with pure sodium carbonate, and projected by small portions at a time into pure potassium cyanide, kept in a state of fusion in a white unglazed crucible. The chloride is rapidly reduced to the metallic state; the crucible is then allowed to cool, and the contents exhausted with water. The resulting ingot of metal is well boiled in water, dried and fused in an unglazed porcelain crucible with free access of air, stirred with a porcelain rod to facilitate oxidation, and finally cast in a porcelain mould. It may be preserved under water which has been boiled to expel the air.

b. Ordinary metallic thallium is fused in contact with the air, in an iron crucible, made nearly red-hot, and then poured into water. The granulated metal is then exposed moist to a warm atmosphere to facilitate oxidation, the oxide being continually removed by boiling out with water. When a considerable quantity of oxide (mixed with carbonate) has been obtained, the solution is heated to ebullition and a rapid current of carbonic acid gas passed through until the liquid is quite cold and the excess of thallium carbonate has crystallised out. The resulting salt is recrystallised and divided into three portions. One portion is projected into pure potassium cyanide kept in a state of fusion, in a porcelain crucible at a dull-red heat; carbonic acid escapes with effervescence, and the metal is reduced to the metallic state. The whole is then allowed to cool, the soluble salts boiled out with water, and the lump of thallium fused in a lime crucible and cast in a lime mould as described farther on.

c. Thallium carbonate, obtained as in process *b*, is covered with a small quantity of water, and decomposed by the current from six of Grove's cells. Much thallium peroxide is deposited, which is removed¹ and preserved for the preparation of thallium by another method. The reduced thallium is then squeezed into a hard cake, melted in a lime crucible, and cast in a lime mould.

d. A third portion of thallium carbonate, obtained as in process *b*, is crystallised several times from water, carbonic acid being passed through during the cooling of the solution. After six crystallisations the carbonate is perfectly white. It is then placed in a porcelain dish, covered with a little water, and decomposed by four of Grove's cells. The spongy metal is washed, boiled in pure water, tied up in a linen cloth, and compressed between steel plates in a vice. The hard lump is broken up, put into a porcelain crucible and melted, no flux being used. It is constantly stirred up with a piece of unglazed porcelain and cast in a warm porcelain mould.

e. The thallium peroxide obtained by the electrolysis of the carbonate (process *c*) is dissolved in rectified sulphuric acid, evaporated to

¹ The operation requires this thallium peroxide to be constantly removed from the positive pole, or the passage of the current will be retarded and ultimately stopped.

dryness, and heated strongly to decompose any persulphate; it is then dissolved in water and recrystallised twice. The thallium sulphate is then reduced to the metallic state by three of Grove's cells, platinum terminals being employed. The metal is then squeezed into a lump and melted under hydrogen, in a porcelain crucible, and cast in a cold polished steel mould.

f. Thallium chloride, as obtained by method *a*, is boiled in nitric acid till most of it is converted into sesquichloride. This is washed by decantation, until it begins to decompose with separation of thallium peroxide, and purified by twice recrystallising.¹ The purified thallium sesquichloride is dissolved in boiling water and poured into dilute ammonia. The precipitated thallium peroxide is washed by decantation till chlorine is no longer detected in the washings, and then boiled in a little water with pure sublimed oxalic acid till the whole is converted into thallium oxalate. This is dried and heated in a crucible until the whole is decomposed into a mixture of metallic thallium and thallium oxide; the reduced metal is then cast in a mould of polished steel.

g. Ordinary thallium is dissolved in nitric acid, the excess of acid driven off by heat, the residue dissolved in water, and the solution is saturated with sulphuretted hydrogen. A slight black precipitate is generally formed, the solution is filtered cold, and is then freed from sulphuretted hydrogen by boiling. Ammonia is then added, which produces a faint precipitate of iron sesquioxide and thallium peroxide; it is then filtered, and the solution is mixed with ammonium oxalate, and concentrated till the thallium oxalate crystallises out. This is freed from ammonium nitrate by recrystallising, and the thallium oxalate decomposed by heat, as in process *f*. The thallium thus obtained is again fused in a lime crucible, a blowpipe flame being directed downwards on to the surface of the fused metal for about 5 minutes, till the slag unites with the lime, forming a semi-fluid pasty mass. The metal is then cast in a lime mould, washed when cold, and kept under boiled distilled water or very dilute acetic acid.

Purification of Thallium by Fusion in Lime.

A piece of well-burnt, very dense quicklime, prepared from black marble, is cut out so as just to fit a porcelain crucible; a hole is then bored in the centre of the lime, and a lump of lime cut to form a stopper. This arrangement is then raised to a temperature above the melting-point of thallium over a gas-burner, and the cavity in the lime is gradually filled with the metal introduced in lumps. The stopper is then put on, and the heat raised to dull redness and kept so for half an hour; after which the melted metal is poured into a lime mould and preserved in a well-stoppered bottle under boiled water or very dilute acetic acid.

¹ A little thallium peroxide is separated each time the sesquichloride is dissolved.

Detection of Thallium by the Blowpipe.

In a closed tube thallium melts easily, and a brownish-red vitreous slag, which becomes pale yellow on cooling, forms round the fused globule.

In the open tube fusion also takes place on the first application of the flame, whilst the glass becomes strongly attacked by the formation of a vitreous slag, as in the closed tube. Only a small amount of sublimate is produced; this is of a greyish-white colour, but under the magnifying-glass it shows in places a faint iridescence.

On charcoal, *per se*, thallium melts very easily, and volatilises in dense fumes of a white colour, streaked with brown, whilst it imparts at the same time a vivid emerald-green colouration to the point and edge of the flame. If the heat be discontinued the fused globule continues to give off copious fumes, but this action ceases at once if the globule be removed from the charcoal. A deposit, partly white and partly dark red, of oxide and teroxide is formed on the support; but, compared with the copious fumes evolved from the metal, this deposit is by no means abundant, as it volatilises at once where it comes in contact with the glowing charcoal. If touched by either flame it is dissipated immediately, imparting a brilliant green colour to the flame border. The brown deposit is not readily seen on charcoal; but if the metal be fused on a cupel, or on a piece of thin porcelain or other non-reducing body, the evolved fumes are of a brownish colour, and the deposit is in great part brownish black. It would appear, therefore, to consist of thallium peroxide rather than of a mixture of metal and oxide. On the cupel, thallium is readily oxidised and absorbed. It might be employed, consequently, in place of lead in cupellation; but to effect the absorption of copper or nickel a comparatively large quantity is required. When fused on porcelain the surface of the support is strongly attacked by the formation of a silicate, which is deep-red whilst hot and pale-yellow on cooling.

The teroxide evolves oxygen when heated, and becomes converted into thallium oxide. The latter compound is at once reduced on charcoal, and the reduced metal is rapidly volatilised with brilliant green colouration of the flame. The chloride produces the same reaction, by which the green flame of the thallium may easily be distinguished from the green copper flame, the latter, in the case of cupreous chlorides, becoming changed to azure blue. With borax and phosphorus salt thallium oxides form colourless glasses, which become grey and opaque when exposed for a short time to a reducing flame. With sodium carbonate they dissolve to some extent, but on charcoal a malleable metallic globule is obtained. The presence of sodium, unless in great excess, does not destroy the green colouration of the flame.

Thallium alloys more or less readily with most other metals before the blowpipe. With platinum, gold, bismuth, and antimony respec-

tively, it forms a dark grey brittle globule. With silver, copper, or lead, the button is malleable. With tin, thallium unites readily, but the fused mass immediately begins to oxidise, throwing out excrescences of a dark colour, and continuing in a state of ignition until the oxidation is complete. In this, as in other reactions, therefore, the metal much resembles lead.

Estimation of Thallium as Platino-Chloride.

Thallium forms an insoluble platino-chloride, which may be used for its estimation. The salt has the disadvantage, however, of being difficult to collect on a filter, as it has a great tendency to run through. This salt is precipitated in the form of a very pale yellow crystalline powder when platinum bichloride is added to an aqueous solution of a salt of the thallium protoxide. When heated to redness, it leaves an alloy of thallium and platinum, the latter metal continually volatilising until, after being kept for some time at nearly a white heat, the platinum is almost free from thallium. This is the most insoluble thallium salt yet met with, one part requiring no less than 15,585 parts of water at 60° F., or 1948 parts of boiling water to dissolve it. It may be useful to compare the solubilities of this compound with that of the corresponding potassium, ammonium, rubidium, and cesium salts.

One Part of Chloro- platinate of—	Water at 60° F.	Boiling Water
Potassium dissolves in . .	108 parts . .	19 parts
Ammonium " . .	150 " . .	80 "
Rubidium " . .	740 " . .	157 "
Cesium " . .	1308 " . .	261 "
Thallium " . .	15585 " . .	1948 "

Estimation of Thallium as Iodide.

This compound is readily formed by double decomposition between an alkaline iodide and a salt of the thallium protoxide, precipitating as a beautiful yellow powder, rather darker than sulphur. Thallium iodide is very difficultly soluble in water, requiring 4453 parts of water at 63° F., or 842.4 parts of boiling water to dissolve it. In analysis it should be collected on a weighed filter and washed with dilute alcohol.

Estimation of Thallium as Sulphide.

From neutral solutions of thallium nitrate, sulphate, or chloride, sulphuretted hydrogen precipitates only a small portion of the metal as a grey-black sulphide. If other metals are present which are completely precipitated by this gas, they carry down larger quantities of thallium. Solutions of thallium acetate, oxalate, or carbonate are completely precipitated. Ammonium sulphide precipitates all thallium salts, forming a brownish-black, dense, flocculent precipitate; if present in small quantities only, the minute particles of sulphide suspended

in the liquid quickly collect together into a few large clots at the bottom of the vessel, leaving the solution quite clear. On filtration the sulphide oxidises in the air, and whilst being washed, unless the washing water contains a little ammonium sulphide, a considerable quantity of the precipitate will be converted into thallium sulphate, which passes through into the filtrate. After drying in hydrogen, it still oxidises on exposure to the air. The higher compounds of thallium appear to be reduced to the state of protosulphide by ebullition with an excess of ammonium sulphide. Precipitated thallium sulphide is readily soluble in dilute sulphuric or nitric acid, and is insoluble in ammonium sulphide or potassium cyanide. This is not a good form in which to separate thallium for quantitative purposes, owing to the difficulty of weighing thallium sulphide without oxidation.

Volumetric Estimation of Thallium.

The ease with which thallium passes from one degree of oxidation to another gives us a means of estimating the metal volumetrically by potassium permanganate. When a solution of this salt is added to a hot solution of thallium protochloride it is instantly decolourised. The termination of this reaction is much more easily seen in the case of thallium than with iron. To be sure of success, the thallium must be present in the solution in the state of chloride, or, at all events, with an excess of hydrochloric acid. It is necessary besides to bring back the thallium always to the state of protochloride, which is very quickly done by adding some sulphurous acid. The solution must be boiled to get rid of the excess of the latter, and then the estimation may be proceeded with. In consequence of the little solubility of the protochloride, it is necessary to have about $\frac{1}{2}$ litre of water to 1 gramme of the salt. The solution of potassium permanganate must be more dilute than that used for estimating iron.

The solution of the permanganate may be titrated by means of pure iron, or by a crystallised stable compound of thallium, such as the sulphate.

0.884 gramme of pure thallium is dissolved in sulphuric acid, the solution diluted with $\frac{1}{2}$ litre of water, a few cubic centimetres of hydrochloric acid added, and some drops of sulphurous acid, to make certain of the degree of oxidation of the thallium. After boiling for half an hour to drive off the sulphurous acid, allow it to cool a little, and then add the permanganate; it is necessary to employ 27.8 c.c. To ascertain the degree of oxidation to which the thallium passes in this reaction, dissolve 0.871 gramme of pure iron, and add the permanganate with the usual precautions. Suppose 21.5 c.c. are required. By bringing up these figures to the equivalents of thallium (208) and of iron, we find that—

2.08 of thallium require	63 c.c. of permanganate
0.28 of iron requires	16 „ „

One of thallium therefore requires four times more oxygen than one of iron, and as one of iron requires half an equivalent of oxygen to pass from the protoxide into the sesquioxide, so one of thallium takes two of oxygen, and passes consequently from the state of protoxide into the peroxide or rather perchloride.

Separation of Thallium from Lead.

In analytical operations, these metals may be separated like thallium and bismuth; or the lead may be precipitated as sulphate, whilst the thallium sulphate will remain in solution. Sulphuretted hydrogen in an acid solution will also precipitate the lead, and leave the thallium dissolved. If the metals are in the form of insoluble salts, boil the mixture in aqua regia, which will convert the thallium into the perchloride and will leave most of the lead in the insoluble condition. The small quantity of lead which gets into solution is easily separated by the addition of a few drops of sulphuric acid.

Separation of Thallium from Cadmium.

These two metals frequently occur together. The thallium may be detected by adding potassium bichromate and then excess of ammonia to the acid solution of these metals: the insoluble thallium chromate will then be precipitated.

Sulphuretted hydrogen passed into an acid solution of these two metals only precipitates the cadmium.

Potassium iodide added to a neutral solution only precipitates the thallium.

Commercial cadmium sulphide, as sold for artists' use, varies considerably in tint, some specimens being of a much deeper orange than others. Thallium is frequently present in the dark-coloured varieties, and it is therefore not improbable that the variations of colour in cadmium sulphide are due to traces of thallium. As an instance of a highly thalliferous cadmium sulphide, I may especially mention a beautiful specimen from Nouvelle Montagne, which formed a prominent object in the Belgian Department of the Exhibition of 1862.

Separation of Thallium from Copper.

When these two metals occur together analytically, they may be easily separated by adding to the acid solution sulphurous acid in excess, and then potassium iodide; a dirty white precipitate will fall, consisting of copper sub-iodide and thallium iodide. On adding ammonia to the washed precipitate, the copper iodide rapidly dissolves, with absorption of atmospheric oxygen, to a deep blue liquid, whilst the thallium iodide is left behind as an insoluble yellow powder.

When potash is added to a solution of copper and thallium protoxides, copper oxide alone is precipitated.

Sulphuretted hydrogen in an acid solution also separates the copper, but as metallic sulphides are very liable to carry down thallium sulphide it is preferable to use other means of separation, if sulphuretted hydrogen can be avoided.

When present, even in small quantities, thallium diminishes the malleability and ductility of copper. Copper prepared in Spain by the cementation process described at page 871, frequently contains considerable quantities of thallium. A specimen, for which the author is indebted to his friend the late Dr. Matthiessen, which had a conducting power for electricity of about 15 (that of pure copper being 100), was found to contain a large quantity of thallium; it is probable that the pre-eminently bad quality of this copper is thus to be accounted for.

Separation of Thallium from Mercury.

Mercury frequently accompanies thallium in the flue-dust from pyrites burners. From mercury per-salts the gradual addition of potassium iodide effects a ready separation. If much mercury is present, the precipitate is almost pure scarlet, but on further addition of potassium iodide drop by drop, the mercury iodide dissolves and leaves the insoluble yellow thallium iodide.

Sulphuretted hydrogen passed through an acid solution of the two metals precipitates the mercury as sulphide. This, however, carries a little thallium down with it.

Separation of Thallium from Silver.

Sulphuretted hydrogen in an acid solution precipitates the silver. If the two metals have been precipitated together as chlorides, boil the mixture in nitro-hydrochloric acid; this will dissolve out the thallium in the form of sesquichloride. Dilute with water, boil, and filter whilst hot. Wash the residue on the filter with hot dilute hydrochloric acid. From the solution thallium sesquichloride separates, on cooling, in the form of orange-yellow crystals.

Silver and thallium chlorides can also be separated by boiling in water. When hydrochloric acid, or a soluble chloride, is added to a solution of the thallium protoxide or one of its soluble salts, a white curdy precipitate of thallium protochloride is thrown down, scarcely to be distinguished at first sight from silver chloride. When boiled in water it, however, dissolves like lead chloride, and separates again on cooling; the crystals, however, are much smaller and less brilliant than those of lead chloride. One part of the chloride dissolves in 288.4 parts of water at 60° F., and in 52.5 parts of boiling water. When boiled in nitric acid or aqua regia, it is converted into the sesquichloride, which separates, on cooling, in yellow crystalline scales. It is soluble in 880.1 times its weight of water at 60° F., and in 52.9 parts of boiling water. Pure water produces a slight decomposition into teroxide and protochloride, which, however, may be prevented by the

addition of a drop of nitric or hydrochloric acid. From the slight solubility of the chlorides, in even boiling water, it is evident that this method of separating thallium from silver is tedious, and is very liable to leave thallium behind.

The best method of separating silver and thallium, when together as chlorides or iodides, consists in reducing the metals by the addition of a rod of pure zinc to the mixture. When the reaction is complete, remove the zinc, and wash with hot water till the washing waters are free from chlorine. Then heat with dilute sulphuric acid, which dissolves the thallium and leaves the silver, or dissolve the whole in nitric acid and precipitate the silver with sulphuretted hydrogen.

Separation of Thallium from Nickel, Cobalt, or Manganese.

Add sodium sulphite in excess to the solution, so as to be certain that all the thallium is in the state of proto-salt, then add excess of sodium carbonate and boil. The thallium will remain in solution, whilst the other metals will be precipitated. Filter off and add potassium iodide to the filtrate; this will precipitate insoluble thallium iodide in the form of a yellow powder. When the thallium is present in traces only, it is better to add potassium iodide direct to the liquid, without separating the other metals with sodium carbonate.

Separation of Thallium from Iron.

Certain kinds of iron pyrites constitute the richest natural source of thallium. At page 372 the methods of separating thallium from thalliferous pyrites on the large scale are fully described. Thallium may be readily detected in thalliferous pyrites in the following manner:—Dissolve the finely powdered mineral in nitro-hydrochloric acid; evaporate with excess of sulphuric acid until the nitric acid is evolved; dissolve in water; and add sodium sulphite to reduce the iron and thallium to the state of proto-salts. On adding potassium iodide, and allowing the liquid to stand for some time, a bright yellow precipitate of thallium iodide will separate. This test is sufficiently delicate to show thallium in a few grains of a pyrites which does not contain more than 1 part in 10,000.

If the iron only is in the state of peroxide (as in the case of thallium-iron alum) the separation may be effected by ammonia, which precipitates the iron sesquioxide and leaves the thallium in solution.

Separation of Thallium from Zinc.

Thallium is present in many specimens of blende and calamine, especially from Nouvelle Montagne and the neighbourhood of Spa, in Belgium. In such cases it accompanies the zinc in most of its preparations, and may, therefore, be frequently detected in the commercial metal. By proceeding in the following manner, the black residue which is left behind when zinc is dissolved in sulphuric acid will

generally be found to contain thallium. Dissolve the residue in nitric acid; evaporate the solution with excess of sulphuric acid; dissolve the residue in a small quantity of water; filter the liquid from lead sulphate and add sodium sulphite. Upon adding potassium iodide to the solution the thallium will be precipitated.

When thallium is present in larger quantities, precipitate the zinc with sodium carbonate, which has no action on thallium.

Separation of Thallium from Chromium.

The thallium chromates are insoluble in water, but readily soluble in hydrochloric acid, chlorine being evolved and a soluble perchloride being produced. When boiled with hydrochloric acid and alcohol, these chromates are quickly decomposed, thallium protochloride being precipitated, whilst chromium sesquichloride remains in solution. Filter off and wash with alcohol, in which thallium protochloride is insoluble.

Separation of Thallium from Gallium.

This separation is not effected satisfactorily by precipitating the alcoholic solution with potassium iodide, as thallium remains in the filtrate and sensible traces of gallium in the deposit. It is not more advantageous to reduce the thallium to the metallic state by means of a sheet of zinc. There are thus introduced into the analysis the impurities so frequently contained in zinc, and the thallium carries down gallium, unless the liquid is kept sufficiently acid, but then the precipitation of the thallium is incomplete. The eight following procedures may be recommended, though in different degrees:—

1. Boiling after supersaturation with ammonia gives good results with thallium sulphate, chloride, or nitrate, if slightly acid. The salts must previously be reduced to the lowest stage of oxidation by the addition of a few drops of a solution of sulphurous acid. If slight traces of thallium remain in the precipitate they are entirely eliminated by repeating the boiling with ammonia; the gallium oxide obtained then gives no spectroscopic indication of thallium.

2 and 8. Calcium and barium carbonates precipitate gallium in the cold without rendering the thallium insoluble beyond slight traces, which disappear entirely during the operations for removing the lime or baryta. Before adding the carbonates the liquid is reduced by means of sulphurous acid.

4. Calcium carbonate may be used in heat after reduction by means of sulphurous acid. There are sensible traces of thallium in the precipitate, but they are subsequently eliminated along with the lime.

5 and 6. Cupric hydrate, as also metallic copper and cuprous oxide, are the best reagents, for the gallium is totally precipitated without carrying down a trace of thallium. If cupric hydrate is employed,

the thallium salts must previously be reduced to the lowest stage of oxidation by means of sulphurous acid.

7. If the quantity of thallium is not too considerable, so that its chloride remains dissolved, gallium may be precipitated by potassium ferrocyanide in a very acid solution and at a temperature of 70°. Traces of thallium contaminate the deposit, which is redissolved in a small excess of potash; there are added to the liquid a few drops of ammonium sulphide recently prepared, and the whole is filtered to separate thallium sulphide. The clear solution is evaporated to a small bulk, supersaturated with a large excess of hydrochloric acid, and mixed with a little ferrocyanide. The slight traces of gallium carried down by the small quantity of thallium sulphide may generally be neglected. If needful, they may be separated by known methods.

8. Thallium may be thrown down by platinum chloride from an alcoholic solution, acidified with hydrochloric acid. A prolonged current of sulphuretted hydrogen removes the platinum contained in the liquid, from which is afterwards obtained gallium containing merely traces of thallium. The chloro-platinate, suspended in water acidified with hydrochloric acid, is treated with hydrogen sulphide, which renders the platinum insoluble. The thallium salt obtained does not contain sensible traces of gallium.

INDIUM.

Preparation of Indium from Commercial Zinc.

Zinc from the Freiburg mines contains, besides a small quantity of lead, iron, arsenic, and cadmium, 0.0448 per cent. of indium. To separate the indium the zinc is dissolved in dilute sulphuric or hydrochloric acid, and boiled until the evolution of gas ceases. The metallic precipitate left, when the precaution is taken to leave a little zinc undissolved, contains all the indium, together with the lead, &c. In the case of a solution containing indium—such as zinc chloride—the separation may be effected by means of sodium acetate, indium having the property, like iron, of forming an insoluble basic salt. A little dilute sulphuric acid is first added to the solution containing indium, and sodium carbonate is next added until, after stirring, a slight cloudiness remains; sodium acetate is then added, and the mixture is boiled. In this way a basic indium sulphate, containing a little iron and zinc, is precipitated. It is best to wash the precipitate by decantation, as the gelatinous precipitate rapidly clogs up the pores of filtering-paper.

From a hydrochloric or nitric solution of indium the separation may be effected by barium carbonate, which perfectly precipitates the oxide in the cold. The precipitate usually contains some iron, but no zinc.

Preparation of Indium from Blende.

Roast the indiferous blende and boil in dilute sulphuric acid; filter, nearly neutralise with sodium carbonate, and then put clean plates of zinc into the solution. Scrape the reduced metals from time to time from the zinc, and preserve the precipitates separately. The purification of the indium is then easier in consequence of this fractional precipitation.

Purification of Indium.

To obtain the indium pure, the precipitate containing it is dissolved in nitric acid. Most of the lead is first removed by means of sulphuric acid; sulphuretted hydrogen is then passed through the liquor until the remainder of the lead, with the arsenic, cadmium, &c., is precipitated. The excess of sulphuretted hydrogen is then got rid of by boiling, and the liquor is next oxidised by means of potassium chlorate and precipitated by excess of ammonia. In this way a good deal of the zinc present passes into solution; a small quantity, however, remains with the precipitated iron and indium oxides. The precipitate is now dissolved in dilute acetic acid, and again precipitated by sulphuretted hydrogen. A little zinc and iron still go down with the indium, and will after six precipitations; so, for the perfect purification, an additional operation is necessary. The mixed sulphides are dissolved in hydrochloric acid; in this solution the ferric chloride is reduced to ferrous chloride by the evolution of sulphuretted hydrogen. Barium carbonate is now added, and then after 12 or 24 hours all the indium is found in the precipitate, free from all impurities but barium.

To obtain the metal, the oxide is carefully heated in a stream of hydrogen. In consequence of the volatility, the heat at first must not be great, and the stream of gas must be passed slowly. After the reduction the metal will be found in small silver-looking buttons, which can be fused together under potassium cyanide.

Separation of Gallium from Indium.

Indium ferrocyanide, being relatively very soluble (especially at 60° to 70°) in a hydrochloric liquid containing from $\frac{1}{3}$ to $\frac{1}{2}$ of the concentrated acid, potassium ferrocyanide may be used for extracting moderate quantities of indium mixed with much gallium. Yet, gallium ferrocyanide retains sensible traces of indium, and the operation needs to be repeated if we wish to obtain an exact separation. This inconvenience, and that of introducing iron into the analysis, render the process somewhat long and difficult. It is only to be recommended when we wish to separate other metals, such as aluminium and chromium, along with a little indium.

Of all the methods tried, the following is the only one which effects a prompt and accurate separation:—The solution, suitably con-

centrated, is treated with a slight excess of boiling potash. The boiling is kept up for some minutes, for in the cold indium oxide is not immediately thrown down by potash. The precipitate retains merely very slight traces of gallium, which are entirely eliminated by one, or at most two, repetitions of the same treatment. The potassic solutions contain merely slight traces of indium which may be neglected in weight if the masses of gallium and indium are small, and consequently the volume of the alkaline liquids is moderate. To extract these traces of indium the solution is supersaturated with a very slight excess of hydrochloric acid, and the gallium and indium are precipitated together by slowly boiling the liquid after supersaturation with ammonia, or better still, by means of cupric hydrate. The gallium and indium chlorides are transformed into slightly acid sulphates; a quantity of ammonium sulphate is added, slightly larger than what is necessary to transform all the gallium sulphate into gallium alum, and the liquid is then concentrated to a very small volume. After cooling, whether crystals of alum are already formed or not, the solution is mixed with 4 to 5 times its volume of alcohol at 70 per cent. The agitation causes the deposit of gallium-ammonium alum in a crystalline powder which is washed once or twice with alcohol at 70 per cent. The alum is then taken up in a little hot water containing a trace of sulphuric acid, and the operation is repeated several times. By far the larger quantity of the gallium is in this manner transformed into ammonium alum free from indium. The alcoholic solutions containing a small quantity of indium and gallium are concentrated down to a small bulk. The oxides are thrown down by boiling with ammonia, or by means of cupric hydrate; they are dissolved in hydrochloric acid, and are then treated with boiling potash. We obtain thus a small supplementary quantity of indium free from gallium. As very little potash suffices, the slight traces of indium in the alkaline solution are absolutely unimportant, though the last residue of gallium may be separated as alum if its quantity is noteworthy. Generally the traces of indium carried by the potash along with the gallium are entirely eliminated after four alcoholic crystallisations of the gallium-ammonium alum. With gallium containing 4 per cent. of indium seven or eight recrystallisations are necessary. These operations are performed very rapidly and easily with the salt derived from less than 0.01 gramme of gallium.

BISMUTH.

For the detection of small quantities of bismuth, Mr. M. M. Pattison Muir recommends Schneider's test liquid prepared as follows:—12 grammes crystalline tartaric acid and 4 grammes stannous chloride are dissolved in caustic potash so as to produce a clear liquid having a distinctly alkaline reaction; it must remain clear at 60°—70° C. To the liquid to be tested is added a considerable quantity of tartaric acid. It

is warmed and made alkaline with caustic potash. A few c.c. of the test liquid are now added, and the mixture is heated for a few minutes to 60°—70°. If bismuth is present a brownish-black colour is produced. One part bismuth may thus be detected in 210,000 parts of liquid. Mercury must be absent; copper and manganese interfere slightly; lead, arsenic, antimony, iron, cobalt, nickel and chromium not at all.

Detection of Minute Traces of Bismuth in Copper.

Sir F. Abel and Mr. F. Field proceed as follows:—About 100 grains of the copper to be examined are dissolved in nitric acid, a solution of lead nitrate, equal to about 5 grains of the salt, is added, and subsequently ammonia and ammonium carbonate. The precipitate is washed with ammoniacal water and dissolved in warm acetic acid. Considerable excess of potassium iodide is introduced, and the liquid is warmed until the precipitate disappears. On cooling, the crystalline scales will show by their colour the presence or absence of bismuth.

If the least trace of bismuth is present, the precipitated scales are no longer yellow, but assume a dark orange or crimson tint, varying in intensity of colour according to the amount of bismuth present. This test is of such extraordinary delicacy that 0·00025 of a grain of bismuth may be detected in copper with the greatest ease, the lead iodide becoming dark orange, while 0·001 grain imparts a reddish-brown tinge and 0·01 grain a bright crimson, the scales resembling silver chromate in appearance.

Detection of Bismuth by the Blowpipe.

The mixture of equal parts of potassium iodide and sulphur recommended by Von Kobell for this excellent test has the great disadvantage of being very deliquescent; even if kept in closely-stoppered bottles it sooner or later becomes pasty, and indeed almost liquid, if the bottles are often opened for use. As it is a great advantage to be able to have such mixtures ready for use, and, where possible, to keep them in little wooden boxes in the portable blowpipe apparatus, Mr. W. M. Hutchings replaces the potassium iodide by cuprous iodide, and finds that, in addition to the advantage of being non-deliquescent, the mixture so made is in other respects superior for use with the test.

Von Kobell's mixture has another disadvantage, viz. that it itself yields a copious *white* sublimate, the brilliant red sublimate obtained when it is used with a substance containing a good deal of bismuth being caused by the mixture of this white with the dark brownish-red given by bismuth iodide alone. When very little bismuth is present and a good deal of the mixture is used, the white frequently overpowers the red almost completely, and when other metals are present which also give white or light-coloured sublimates, it greatly assists in concealing the bismuth colour. This disadvantage is also got rid of by using cuprous iodide and sulphur.

The precipitated cuprous iodide is washed free from all trace of potassium salts, dried perfectly, and then ground up to an intimate mixture with an equal volume, or rather more, of flour of sulphur. This proportion is the best; when less sulphur is used, there is more or less white sublimate of cuprous iodide obtained, and also the formation of bismuth iodide is not as copious. For testing pyrites or other sulphide substances, less sulphur, or even none at all, would be required; but it is best to have a mixture which is equally applicable to all bismuth combinations. This mixture can be kept rammed tight into little wooden boxes, and is always ready for use. On aluminium plate it is decidedly more delicate as a reagent than the potassium iodide mixture, using in each case 2 volumes of reagent to 1 volume of the powdered substance to be tested, intimately mixing to a paste and heating gently on a charcoal slip.

The merest trace of the dark brownish-red bismuth iodide is very conspicuous on the clean aluminium. The plate should be made pretty hot by blowing the flame upon it some distance above the ledge before commencing to heat the test mixture, in order to prevent the settling of a sublimate of *iodine*, or any condensation of moisture, which latter destroys the red bismuth sublimate. This precaution is particularly necessary when very little bismuth is present.

On ordinary charcoal or a blackened porcelain support, the dark-coloured bismuth iodide is not nearly so conspicuous as on aluminium, and does not show so well as the brighter red obtained by using potassium iodide. But a few tests with a substance containing very little bismuth will convince anybody that the aluminium plate, with the cuprous oxide mixture, is very much preferable to charcoal and potassium iodide.

Substances containing mercury, when treated with the iodide mixture on platinum plate, give a sublimate of mercuric iodide which is partly red and partly yellow, the relative quantities of the two colours varying much in sublimate from the same substance. The red is much lighter and brighter than that obtained from bismuth from the cuprous iodide mixture. It might possibly be taken for the bismuth sublimate mixed with that of lead; but as the number of minerals containing mercury is so limited, and the presence of that metal is so easily proved by other tests, no mistake is likely to arise from this cause.

The value of this test of Von Kobell's is very great; it deserves to rank as one of the best—in some cases the best—test for bismuth. As little as 0.2 or 0.1 per cent. can be safely detected by it in many cases, and with great rapidity. In pyritous ores which fuse to a regulus, or in smelted regulus, a considerable amount of bismuth might be present and not be detected by the ordinary sublimate of bismuth oxide, which is frequently very difficult to obtain from such combinations. But a fraction of a per cent. can be found by this test without resorting to the wet way.

Substances containing lead give a copious light yellow sublimate when heated with the iodide and sulphur mixture, and when lead is present beyond certain limits this yellow overpowers the bismuth reaction. According to Cornwall (*Chemical News*, vol. xxvi. p. 150), when lead oxide was mixed with 5 per cent. bismuth oxide, and tested on charcoal by Von Kobell's mixture, the bismuth could only just be detected, and not with distinctness. But when lead oxide containing only 1 per cent. bismuth oxide is tested with the cuprous iodide mixture on aluminium plate, a very fine brownish-red sublimate is always obtained by heating very gently and observing after a few seconds. Later on the yellow covers this up; but the bismuth iodide always comes off first, and can be seen if observed in time. In all cases sublimates must be allowed to get quite cold before judging them; lead iodide is reddish when hot, but pure light yellow when cold.

Cornwall's tests in open glass tubes (*Chemical News*, vol. xxvi. p. 150), which will detect bismuth when present in such small quantity with lead and antimony that the above method fails, can be better applied with the cuprous iodide mixture than with potassium iodide, and so much sulphur as he recommends (5 volumes) does not require to be added.

Volumetric Estimation of Bismuth.

M. Kuhard bases a process upon the precipitation of bismuth, as arseniate, from its nitric acid solution, by adding a measured quantity of standard solution of disodic arseniate in slight excess, and upon the estimation of the amount of residual arseniate by means of standard uranic nitrate. In carrying out the estimation, the nitric acid solution of bismuth under examination must be free from hydrochloric acid, as well as substances precipitable as arseniate. Before entering upon the process of actual analysis, the amount of bismuth in a solution to be examined is approximately ascertained by the same method as that employed in the actual analysis.

A convenient quantity of the solution under examination is taken, a slight excess of disodic arseniate solution, whose exact strength has been previously ascertained by a known weight of bismuth, is added to the solution, which is then agitated well without heating, and the mixture set aside for a time to complete the reaction. The mixture containing the precipitate is rendered slightly alkaline with ammonia and then slightly acid with acetic acid. Now uranium solution, the relative strength of which, as compared with that of arseniate, has been previously ascertained, is allowed to run in from a burette very slowly, the mixture having been constantly well agitated to complete the reaction. The end of the reaction is recognised in the ordinary manner by means of potassium ferrocyanide. From the amount of uranium solution used the excess of arseniate can be calculated; and from the actual amount of arseniate found by subtracting the excess from the whole amount taken, the quantity of bismuth can be easily calculated.

Mr. M. M. P. Muir estimates the metal by precipitating a nearly neutral solution of the nitrate by potassium chromate or dichromate in a manner similar to that proposed by Pearson, but he ascertains the critical point by testing the clear solution from time to time with argentic nitrate until red argentic chromate is produced; the chromium solution being previously titrated with a solution of bismuth of known strength. The presence of chlorine, sulphuric acid, calcium, copper, or arsenic interferes seriously with the results obtained by this method.

Very accurate results are obtained by another process devised by the same author. The nitric acid solution of bismuth is mixed with an excess of sodium acetate, a measured volume—excess—of standardised sodium phosphate is added, the liquid boiled and filtered, the precipitate is well washed with hot water, and the excess of phosphoric acid estimated in the filtrate by titration with a standard solution of uranium acetate.

Another method also due to Mr. Muir is as follows:—An excess of saturated solution of oxalic acid is added to the solution containing bismuth, the precipitate allowed to settle, the supernatant liquid poured off, and the precipitate boiled with water until free from acid. The residue is now dissolved in dilute hydrochloric acid and titrated with permanganate. The absence of free hydrochloric acid must be secured before precipitating. The results are accurate, and the method is generally applicable.

Lastly, in a method proposed by Messrs. Muir and Robbs, the bismuth oxide is dissolved in a minimum quantity of nitric acid, the solution freed from excess of nitric acid by evaporation, and a large excess of acetic acid added. An excess of standard potassium oxalate is added in a measuring-flask, and the double bismuth and potassium oxalate, and allowed to settle. An aliquot portion of the clear solution is drawn off and titrated with permanganate.

Purification of Bismuth.

A simple plan to purify bismuth is based on the fact that when a large quantity of water is added to its solution mixed with hydrochloric acid a completely insoluble precipitate of bismuth oxychloride is obtained. Dissolve the metal in nitric acid and evaporate down with excess of hydrochloric acid; the residue consists of bismuth chloride. Add concentrated hydrochloric acid and heat till the residue is dissolved; filter if necessary through a sand filter. Now pour the solution in a thin stream, with constant stirring, into a large quantity of cold distilled water. A white precipitate of oxychloride is produced, which may either be weighed as such or reduced to the metallic state by fusion with potassium cyanide.

Detection of Calcium Phosphate in Bismuth Subnitrate.

Calcium phosphate is sometimes met with in bismuth subnitrate as an adulterant. It may be easily detected in the following way :—

To 1 part of the bismuth salt dissolved in weak nitric acid add 2 parts of citric acid ; dissolve with the aid of a little water ; add an excess of solution of ammonia, and boil. Any phosphate present will be thrown down by continuous boiling of the solution.

Separation of Bismuth from Thallium.

These elements frequently occur together in minerals containing bismuth, and thallium may frequently be detected in medicinal preparations of bismuth, especially the carbonate. The bismuth compound is to be first obtained in the form of a dilute solution, any convenient acid being used for this purpose. A slight excess of sodium carbonate is now added, and then a little potassium cyanide free from sulphide. The mixture is to be gently warmed and allowed to stand for 10 minutes, then filtered, and a few drops of ammonium sulphide added to the clear liquid. If the slightest trace of thallium were originally present in the bismuth compound, it will now be precipitated as a sulphide, which, upon gently heating the liquid (not to the boiling-point), gradually collects together in deep brown, almost black, flakes, after the characteristic manner of thallium sulphide.

This process is one of extreme delicacy. By means of it 1 part of thallium can be detected in the presence of more than 10,000 parts of bismuth. In some cases, the thallium is present in so small a quantity as to occasion only a slight darkening of the liquid when the ammonium sulphide is added. Upon allowing this to digest at a gentle heat, it will generally collect in the form of a few flakes at the bottom. These may be collected together on a small filter, washed to the apex, and tested in the spectroscope. When the precipitate is only present in sufficient quantity to produce a faint dark stain on the filter-paper, the latter may be partially dried by pressure between blotting-paper, opened, and the stained surface scraped up with a knife. The dark fibres are now to be twisted up in a platinum wire loop and held in the flame of the spectroscope, when they will give abundant indications of the presence of thallium.

Separation of Bismuth from Gallium.

Three methods are to be recommended :—

1. The distinctly acid hydrochloric solution is saturated with hydrogen sulphide. All the bismuth is obtained as sulphide, which retains no gallium. The operation succeeds even when the liquid has been rendered turbid by a previous dilution.

2. The bismuth may be reduced by zinc in a solution which is kept distinctly acid, but it is better to use copper, which does not introduce

impurities like zinc, and the ulterior separation of which from gallium is easy. The acid hydrochloric solution is treated for from 12 to 80 hours with an excess of finely divided copper. The liquid is kept at a gentle heat all the time, which hastens the deposition of the bismuth. We find no bismuth in the liquid or gallium in the deposit. The formation of insoluble cuprous chloride is not an inconvenience.

8. In a solution containing $\frac{1}{2}$ of its volume of concentrated hydrochloric acid, and in presence of bismuth, gallium chloride is precipitated by potassium ferrocyanide, either in the cold or at 60° to 70°. The gallium ferrocyanide, well washed with hydrochloric water, retains no bismuth. It is to be remarked that, contrary to the statements of the chemical text-books, the precipitate formed by ferrocyanide with bismuth chloride is readily soluble in hydrochloric acid, even if dilute.

Boiling potash does not effect the exact separation of gallium from bismuth. The precipitated oxide is free from gallium, but the alkaline liquid retains a notable quantity of bismuth. It is generally, but erroneously, assumed that in analyses bismuth oxide is completely precipitated by potash.

Separation of Bismuth from Lead.

Add to the concentrated solution just enough hydrochloric acid to precipitate all the lead chloride, but so that a few drops of water do not render the liquid turbid. Then add dilute sulphuric acid, the slow action of which is hastened by occasional agitation; finally, after having added alcohol and well mixed the whole by renewed agitation, allow the lead sulphate to deposit. This precipitate is to be filtered and washed, first with alcohol containing a few drops of hydrochloric acid, and then with pure alcohol. The bismuth may be precipitated in the filtrate by dilution with a large quantity of water.

Estimation of Bismuth in Lead Alloys.—The alloys are dissolved in nitric acid, the solution diluted with water, and the bismuth precipitated by a strip of pure lead. The precipitated bismuth, black in colour and in the state of powder, is quickly washed off the lead, and the solution of lead decanted; the bismuth is then washed, first with water and then with alcohol, filtered on a weighed filter, dried, and weighed.

Separation of Bismuth from Mercury.

To the solution containing the bismuth and mercury (as per-salt) add a large excess of hydrochloric acid to prevent the precipitation of bismuth oxychloride, and then add phosphorous acid. On standing, the mercury will be precipitated in the form of protochloride. After the separation of the mercury add a large quantity of water, which precipitates the bismuth as oxychloride. Reduce this to the metallic state by fusion with potassium cyanide.

**Detection of Copper, Bismuth, and Cadmium when
simultaneously present.**

M. Iles adds to the slightly acid solution of the three metals, potassium ferricyanide in slight excess, when all three are thrown down as ferricyanides. Potassium cyanide is added in excess and the mixture is gently heated. The copper and cadmium compounds dissolve, whilst the bismuth remains as a white flocculent hydroxide. The filtrate is divided into two portions; the one is tested for copper with hydrochloric acid, which occasions a brown-red precipitate of copper ferrocyanide, whilst to the other is added a little ammonia and ammonium sulphide. On the application of a gentle heat, yellow cadmium sulphide is precipitated.

CHAPTER IX.

ANTIMONY, TIN, ARSENIC, TELLURIUM, SELENIUM.

ANTIMONY.

Estimation of Antimony.

WHEN antimony is precipitated in the form of sulphide, instead of weighing it as such, Professor Wöhler advises that it be converted into antimoniate of antimony oxide ($\text{Sb}_2\text{O}_3, \text{Sb}_2\text{O}_5$), by complete oxidation with fuming nitric acid in a weighed porcelain crucible. To avoid ignition, the substance must be moistened with a few drops of dilute acid before adding the fuming acid. A prolonged digestion effects the complete solution of the pulverulent precipitate of sulphur. The excess of acid is then evaporated off carefully, and the residue calcined.

Mr. Sharples employs the following process in the precipitation of antimonious sulphide:—Into the solution, containing, as usual, tartaric and free hydrochloric acid, a current of sulphuretted hydrogen is to be passed, the liquid being, during the passage of the gas, gradually heated to the boiling-point. The boiling is then to be continued for 15 or 20 minutes, the current of gas passing uninterruptedly until the voluminous sulphide has become a dense granular powder occupying but a small portion of the original volume of the sulphide. The sulphide may then be washed with great facility, and dried upon a sand filter at 200° — 300° C. All the estimations of antimony made in the laboratory of the Lawrence Scientific School for some years have been executed in this manner, the results leaving nothing to be desired. Arsenious sulphide does not become granular and dense under the same circumstances.

Detection of Antimony in Sublimates.

In the examination of mineral bodies for antimony, the test substance is often roasted in an open tube for the production of a white sublimate. Dr. E. Chapman, Professor of Mineralogy at Toronto, recommends for the detection of antimony in this substance the following process—a method more especially available when the operator has only a portable blowpipe-case at his command:—The portion of the tube to which the chief part of the sublimate is attached is to be cut off by a triangular file, and dropped into a test-tube containing some tartaric acid dissolved in water. This being warmed or gently boiled, a part at least of the sublimate will be dissolved. Some potassium

bisulphate—either alone, or mixed with some sodium carbonate and a little borax, the latter to prevent absorption—is then to be fused on charcoal in a reducing flame; and the alkaline sulphide thus produced is to be removed by the point of the knife-blade and placed in a small porcelain capsule. The hepatic mass is most easily separated from the charcoal by removing it before it has time to solidify. Some of the tartaric acid solution is then to be dropped upon it, when the well-known orange-coloured precipitate of antimony sulphide will at once result.

In performing this test, it is as well to employ a somewhat large fragment of the test substance, so as to obtain a thick deposit in the tube. It is advisable also to hold the tube in not too inclined a position, in order to let but a moderate current of air pass through it; and care should be taken not to expose the sublimate to the action of the flame, otherwise it might be converted almost wholly into a compound of antimonious and antimonie acids, the greater part of which would remain undissolved in the tartaric acid. A sublimate of arsenious acid, treated in this manner, would, of course, yield a yellow precipitate, easily distinguishable by its colour, however, from the deep orange antimonial sulphide. The crystalline character, &c. of this sublimate would also effectually prevent any chance of misconception.

Dr. A. Weller proceeds as follows for the estimation of antimony:—Antimonie acid and antimonie oxide, and in like manner antimony penta- and trichloride, can be most easily distinguished from each other by their different behaviour with potassium iodide. The property of the former, when in hydrochloric solution, of separating 2 atoms of iodine from potassium iodide for each atom of antimony, can be used for the qualitative estimation of antimony. In order to verify the method, weighed quantities of finely pulverised pure metallic antimony are oxidised in a flask at a gentle heat with potassium chlorate and hydrochloric acid, and the excess of chlorine is expelled by strong heating. The solution of antimony pentachloride thus obtained is introduced into the flask of Bunsen's chlorine distillation apparatus by means of hydrochloric acid, considerably diluted, and mixed with a sufficiency of perfectly pure potassium iodide, avoiding too great an excess. The liberated iodine is distilled into dilute solution of potassium iodide, observing all the precautions laid down by Bunsen, and especially cooling the retort well in flowing water. When cold the distillate is titrated in the usual manner by means of very dilute sulphurous acid and an iodine solution of known strength. The distillation-flask has the capacity of about 120 c.c. The distillation requires from 5 to 10 minutes. Particularly important is the fact that stannic acid and stannic chloride in acid solutions do not decompose potassium iodide. This behaviour renders it possible to estimate antimony in presence of tin, as in alloys, easily and accurately. The tin is calculated as difference.

M. A. Guyard states that when a neutral concentrated solution of

antimony terchloride is mixed with a slight excess of gallic acid, all the antimony is precipitated in the state of a double gallate of antimony teroxide and water.

Even in an acidulated liquor, antimony bigallate is almost completely insoluble, and in the liquor separated by filtration from the precipitate, sulphuretted hydrogen reveals but a minute quantity of antimony which can be neglected for most practical purposes.

In these conditions, antimony is the only metal precipitated by gallic acid. All the other gallates, even those which are insoluble in water, are extremely soluble in the liquor from which antimony has been precipitated, and, consequently, gallic acid affords an easy means of separating at once antimony from the other metals.

It follows, also, that gallic acid is a very perfect precipitating reagent of antimony; in fact, it has only one defect, it is a non-volatile organic acid, and as such it alters the behaviour of some metals with some of their precipitating reagents, so that after the separation of antimony it is sometimes necessary to precipitate by sulphuretted hydrogen or by ammonium sulphide the metals left in the solution. But as this operation would, in many cases, have to be performed for convenience's sake, it matters but very little. On the other hand, most metals can be precipitated, even in presence of an excess of gallic acid, by means of appropriate reagents.

As stated above, the solution of antimony terchloride must be neutral or only slightly acidulated, and, what is most important, the solution must be concentrated. The reason of this is obvious, for antimony bigallate is partially or totally soluble in hydrochloric acid, according to the quantity of this acid present in the liquor, and, as is well known, the weaker a solution of antimony is, the more acid is required to keep it clear, while the more concentrated the solution of antimony is, the more neutral it can be obtained.

After a strong and neutral solution of antimony terchloride has been prepared, only a slight excess of gallic acid should be added.

The solution of gallic acid used for the precipitation of antimony must be quite recently prepared. Antimony bigallate is a very white precipitate, somewhat bulky, but which settles very rapidly. It cannot be washed on the filter, for it invariably passes through as soon as the acidulated mother-liquid has been washed away. But as it settles very rapidly in liquors, the mixed mode of decanting and filtering must be resorted to, and in this instance the process presents neither inconvenience nor difficulty. The only disadvantage is that more washings are obtained than would be the case with simple filtration. For this purpose the precipitate is allowed to settle, the liquor is poured on the double filter and decanted as closely as possible from off the precipitate. This done, the flask holding the precipitate is refilled with hot water, the precipitate is allowed to settle once more, and the supernatant liquor is again filtered and decanted as closely as possible from the

precipitate. The same operation is repeated three or four times; the precipitate is then placed on the filter, where it can be washed once or twice with safety.

The drying of antimony bigallate, with the usual precautions, is very easily effected in the water-bath at the temperature of $100^{\circ}\text{C}.$, and the precipitate thus thoroughly dried contains exactly 40·85 per cent. of metallic antimony.

In the estimation of antimony, the dried bigallate should be weighed as soon as it has cooled, or, better still, shortly after it has been left to cool in a dried atmosphere, for it has a great affinity for water, which it absorbs rapidly from the air.

The estimation of antimony in the state of bigallate dried at $100^{\circ}\text{C}.$ is very accurate indeed when the precautions indicated have been observed. But it is not absolutely necessary to estimate the metal in this state, even after it has been separated as bigallate, for antimony bigallate is extremely soluble in weak hydrochloric acid, so that, after it has been placed on the filter, it is only necessary to dissolve it in hydrochloric acid, to wash well the filter with dilute hydrochloric acid, and to precipitate the solution thus obtained by sulphuretted hydrogen, to be enabled to estimate antimony as usual in the state of tersulphide.

When antimony has been estimated as bigallate, or separated in this state from metals insoluble in ammonium sulphide, an excellent precaution to take to ascertain the perfection of the separation is to dissolve the antimony bigallate which has been used for the estimation of antimony in an excess of ammonium sulphide. There ought to be no residue of black sulphides insoluble in this reagent.

Were it not for the remarkable reaction described below, gallic acid could be used only in very limited instances—in those only in which the antimonial compound dissolved in hydrochloric acid gives at once a solution of antimony terchloride, for solutions of antimony perchloride are quite unfit for the estimation of this metal by gallic acid. But when a solution of antimony perchloride, slightly acidulated with hydrochloric acid, is mixed with potassium iodide, the antimony perchloride is reduced to a state of terchloride.

Whenever there is the slightest doubt about the composition of a solution of antimony obtained, it is only required to heat the solution with a slight excess of hydrochloric acid and a little potassium iodide. When no iodine is evolved, it is because the whole of the antimony exists in the state of terchloride; when iodine is evolved, it is because part or the whole of the antimony exists in the state of perchloride, and it is only necessary to add potassium iodide little by little until no more free iodine is evolved to be certain that the whole of the antimony is reduced to the state of terchloride.

The solutions of antimony terchloride thus prepared and properly concentrated by slow evaporation are then quite ready to be precipitated by gallic acid.

Estimation of Antimony in Native Antimony Sulphide.

The estimation of antimony in this mineral is very easily effected by means of gallic acid, and its complete and accurate analysis is rendered simple by the gallic-acid process.

Twenty grains of the powdered mineral are treated by a slight excess of hydrochloric acid, and the mixture is gently heated until the whole of the sulphuretted hydrogen disengaged is thoroughly evolved. The solution is then filtered, the filter and matrix are washed with dilute hydrochloric acid, and the solution is slowly evaporated in the flask until it is conveniently concentrated and freed from the excess of hydrochloric acid.

In this solution the whole of the antimony exists in the state of terchloride, a slight excess of a recently prepared solution of gallic acid is added, with the precautions already indicated. Hot water is then added, and the precipitate of antimony bigallate is washed, dried, and weighed, as has already been stated. Antimony may also be estimated as sulphide after having been separated as bigallate.

Twenty grains of this mineral are quite sufficient for the estimation of antimony, but in the complete analysis it would be inconvenient to operate upon more than 50 grains, as the precipitated antimony bigallate is very bulky.

Antimony being separated as above, iron, lead, copper, silver, arsenic, and sometimes zinc, cobalt, and other metals remain in solution.

Arsenic exists much less frequently than is generally supposed. Copper is very often present. It can be estimated here with the greatest accuracy, as the whole of it exists, or may be made to exist, in the filtrate.

The analysis of the filtrate is proceeded with as that of an ordinary liquor containing the metals mentioned. The only metal which cannot be properly estimated in this liquor is iron, the presence of gallic acid preventing its precipitation, even by means of ammonium sulphide, but its complete separation from antimony is so simple by the known methods that this fact need only be mentioned.

Estimation of Antimony in the Antimony Sulphide obtained in the Course of Analysis.

In the course of a complicated analysis, it is often absolutely necessary to obtain antimony first in the state of a sulphide mixed with a large quantity of sulphur, and contaminated with copper, arsenic, or tin sulphides.

The gallic-acid process affords a simple means of carrying out a careful analysis in this part of the operation, and of estimating antimony by a direct process.

For this purpose the collected mixture of sulphur, antimony sul-

phide, &c. wet or dried, is first of all treated by hydrochloric acid, and when the action has ceased a little potassium chlorate is added, to attack any copper or arsenic which might have escaped the action of the acid. The solution thus obtained decanted from off the residue of sulphur is evaporated, reduced by potassium iodide, and precipitated by gallic acid. In all this the mode of proceeding is identical with the process fully explained in the next example.

Separation of Antimony from Mercury.

These metals can readily be separated by precipitating the mercury as protochloride by hydrochloric acid and phosphorous acid, according to the plan previously described, the antimony being retained in solution with tartaric acid, which does not prevent the precipitation of the mercury protochloride.

TIN.

Estimation of Tin Protoxide.

Tin protoxide dissolved in potash possesses the property of reducing cupro-potassic tartrate in the same way as glucose. The sensibility of this reagent is very great, as minute traces of tin protoxide suffice to determine a deposit of copper protoxide.

The solution containing tin protoxide is treated with a slight excess of potash, so as to redissolve the precipitate first formed; cupro-potassic tartrate is added to the alkaline solution and the whole boiled; a precipitate of copper protoxide instantly forms. When only traces of tin oxide exist in the liquid, the precipitate may not be apparent in the first few moments, but it collects, and becomes perfectly visible after standing 10 or 12 hours. During this reaction, the tin protoxide passes to the state of stannic acid, and no longer reacts on the cupro-potassic reagent.

One equivalent of tin protoxide reacting on two equivalents of copper binocide precipitates one equivalent of copper protoxide.

In other words, one part by weight of copper protoxide obtained by the reduction of cupro-potassic tartrate corresponds to 0.987 of tin protoxide, or 0.825 of metallic tin. Arsenious acid, dissolved in potash, also reduces the cupro-potassic reagent, changing, meanwhile, to arsenic acid. Reduction does not take place so rapidly as with tin protoxide; it is, however, complete. One equivalent of arsenious acid, while changing to arsenic acid, reacts on four equivalents of copper binocide, precipitating two equivalents of copper protoxide.

One part of copper protoxide, obtained by reducing the cupro-potassic reagent, corresponds to 0.692 of arsenious acid, or 0.524 of metallic arsenic.

No other metallic oxide soluble in potash exercises any action on the cupro-potassic reagent.

Estimation of Tin Binoxide.

Tin when in the state of bichloride may be estimated volumetrically by precipitation with a standard solution of potassium ferrocyanide; the operation is carried out in a similar way to the estimation of lead by potassium ferrocyanide (see page 847).

Mr. A. H. Allen finds that metastannic acid is soluble in hydrochloric acid, and that any method of analysis depending on its supposed insolubility in hydrochloric acid must be utterly worthless. The presence of stannic phosphate or arseniate in no way alters the solubility of metastannic acid, but renders the solution liable to precipitate on addition of water, especially when heated. The residue left when antimony has been oxidised by nitric acid is perfectly soluble in hydrochloric acid, but of course the solution is very readily precipitated by dilution. Metastannic acid readily and completely dissolves when heated with concentrated sulphuric acid, becoming converted into *ordinary* stannic sulphate. If the liquid be poured into cold water, a solution of stannic sulphate is at first obtained, but this quickly deposits some of the tin as *ortho*-stannic hydrate. On boiling the solution of stannic sulphate, the whole of the tin is precipitated as metastannic acid.

Ignited and native stannic oxides are not completely dissolved by hot strong sulphuric acid. Fusion with acid potassium sulphate acts on them more or less perfectly, and the aqueous solution of the product contains stannic sulphate, giving a precipitate of metastannic acid on boiling. The reaction presents the closest analogy to the decomposition of titanate sulphate by dilution and boiling.

On adding about twice its bulk of hydrochloric acid to the solution of metastannic in sulphuric acid, a solution is formed which will bear considerable dilution without suffering precipitation. This liquid corresponds in every respect to a solution of *ordinary* stannic chloride, and is free from *meta*-chloride.

The residue left on oxidising antimony by nitric acid is readily acted on by strong sulphuric acid; but the solution produced by subsequent treatment with hydrochloric acid is very readily precipitated by water. Of course this can be avoided by the addition of tartaric acid. Ignited antimonious acid is not dissolved by heating with sulphuric acid.

On making the observation that ordinary stannic sulphate was formed when metastannic acid was heated with concentrated sulphuric acid, the value of the reaction for analytical purposes became at once apparent.

The reaction is especially serviceable in analysing the residue left on dissolving alloys in nitric acid. The following are the details of the method:—

The residue is washed, and heated with concentrated sulphuric

acid in moderate quantity until copious fumes of the acid are evolved. The liquid, which should be quite clear, is allowed to cool, and is then treated with 2 or 3 times its bulk of concentrated hydrochloric acid, and boiled if not still perfectly clear. The solution is diluted with about an equal bulk of water, and is then ready for examination. Estimation of the metals can be effected by the usual processes. For their detection the following method is preferable. The solution is divided into several portions.

1. Is tested for antimony with zinc in a platinum vessel, or by heating with a fragment of metallic tin (this precipitates copper also, if present).

2. Is diluted and tested for iron and copper by potassium ferrocyanide.

3. Is diluted, treated with tartaric acid, excess of ammonia, and 'magnesia mixture,' stirred, left some hours, and the sides of the vessel carefully examined for streaks of ammonio-magnesium phosphate or arseniate; these, if detected, may be readily distinguished by the method described in the *Chemical News*, xxiv. p. 120. Small quantities of arsenic are difficult of detection by magnesium, owing to the solubility of the ammonio-magnesium arseniate in ammoniacal liquids. Direct application of the molybdic acid test to the acid liquid often indicates the phosphate or arseniate when present, but it is not to be relied on.

4. The solution is boiled (without dilution) with a few inches of soft iron wire until colourless. It is then diluted with about 2 parts of water and again heated for a few minutes. By this means the tin is completely or partially reduced to the stannous condition, without being precipitated in the metallic state as when zinc is used; the solution decanted from the precipitated antimony (and copper), and the tin at once detected by mercuric chloride (which is not reduced by ferrous chloride), or the brown stannous sulphide may be precipitated by hydrosulphuric acid. Mere traces of tin may be detected in this manner.

Assay of Tin Ores.

1. Mr. J. W. B. Hallett has found that tin-stone is very easily resolved by fusion with 3 or 4 times its weight of potassium hydric fluoride. The mineral must be finely pulverised. The fused mass is treated directly in the crucible with sulphuric acid to expel fluorine, after which, by adding water, filtering, and boiling the filtrate, the whole of the tin is thrown down as stannic acid, which is to be separated from traces of iron in the usual manner. This method of resolving the ore of tin is much more convenient than fusion with caustic alkalies, or with sulphur and sodium carbonate.

2. M. Moissenet precipitates the metal from a solution of the chloride by means of zinc, and then melts the precipitated metal in stearic acid. His process comprises five operations:—

- I. Purification of the ore by treatment with aqua regia.
- II. Reduction of the residue in the presence of charcoal.
- III. Solution of the tin and iron in hydrochloric acid.
- IV. Precipitation of the tin by means of zinc.
- V. Fusion of the precipitate into a button in stearic acid.

The precipitation of tin by zinc is very rapid, and takes place in strongly acid solutions; but the amount of acid and the dilution of the chloride influence the condition of the precipitate. In some solutions it appears in brilliant needles, but in very dilute solutions, and always towards the end of an operation, it is only a muddy deposit. The author recommends that a button of zinc be suspended in the liquid by means of a copper wire. When the precipitation is finished the metal is collected and pressed into a porcelain capsule. The lump so formed is melted in a few minutes if a piece of stearine is added to it.

8. Referring to the well-known difficulty of obtaining all the tin in one button in a dry assay by the ordinary process, and the error of 5 or 10 per cent. which may arise, M. C. Winkler suggests the addition of copper for the purpose of collecting together the tin.

The ore is finely pulverised and roasted, first by itself and then once or twice with charcoal or coke, to remove sulphur, arsenic, and antimony. The residue is then digested for a quarter or half an hour with hot hydrochloric acid, and afterwards well washed with hot water. Iron, manganese, and copper are more completely removed by fusion with potassium bisulphate, and then treating with hydrochloric acid, and washing with water. Tungstic acid, if present, will now be removed by digesting with caustic potash or ammonia.

The tin oxide, silica, &c. remaining are now mixed in a crucible with an equal weight of copper oxide, and 2 or 3 parts of a flux, consisting of 2 parts anhydrous sodium carbonate, 1 part white flour, and $\frac{1}{4}$ part borax glass. The whole is covered with a layer of common salt, upon which a piece of charcoal is laid. The crucible is heated first to a red and then to a dull white heat for an hour, after which a button containing the whole of the tin and copper reduced will be found at the bottom.

As pure copper oxide may not be obtainable, a portion of every sample should be separately assayed. The weight of the tin will be found by subtracting the weight of the copper from that of the button.

4. The most uniformly successful process for the assay of tin ores has been found by the author to be the following:—The sample having been carefully selected, is first crushed by the hammer in a steel mortar, and then further reduced to powder in an agate mortar. 100 grains is a convenient quantity to be taken for analysis, and it is always advisable to make two independent experiments upon the same sample of ore, with the view of having a control; the highest result obtained is that upon which to place reliance, since the error must always be on the side of loss rather than excess. A couple of small Hessian crucibles,

of about 3 ounces capacity, are prepared in the first instance by ramming into the bottom of them a small charge of powdered potassium cyanide sufficient to form a layer of about $\frac{1}{2}$ inch in depth; the weighed quantities of tin ore are then intimately mixed with from 4 to 5 times their weight of the powdered cyanide, and the mortar rinsed with a small quantity of the pure flux, which is laid upon the top of the mixture. The crucibles are then heated in a moderate fire or over a gas-blowpipe, and kept for the space of 10 minutes at a steady fusion; they are then removed, gently tapped to facilitate the formation of a single button, and allowed to cool. Upon breaking the crucibles the reduced metal should present an almost silvery lustre, with a clean upper layer of melted flux. The precaution should be taken of dissolving the latter in water for the purpose of being satisfied of the absence of any trace of reduced metal or heavy particles of the original ore. There is always contained in the commercial cyanide a sufficient quantity of alkaline carbonate to secure the perfect fusion of the siliceous gangue and other like impurities in the tin ore, but the operator should assure himself of the absence of copper and lead in the ore, either by preliminary treatment with hydrochloric acid, in which tin-stone is absolutely insoluble, or by testing the button of reduced tin, after hammering or rolling, for such metallic admixture. A minute trace of iron has been found in the melted buttons, and sometimes gold, but not so much as to add appreciably to their weight.

This process will sometimes furnish identical results, and when worked with ordinary care it may always be relied upon as giving numbers true to within $\frac{1}{2}$ per cent.

Mr. Peter Hart gives the following method for the rapid estimation of tin in tin ore:—Finely powder in the agate mortar some 20 to 25 grains of the perfectly dry ore; place this in a small test-tube and weigh. Fuse about 4 times this weight of potassium cyanide in a small and rather deep porcelain capsule over a Bunsen burner. When in calm fusion and quite red hot remove the flame and project the ore into this. Now weigh the tube again, and the difference will equal the weight of ore employed, replace the gas-flame, and keep in quick fusion for 15 or 20 minutes, by which time the tin and iron oxides will be reduced to the metallic state, and lie as in a sponge at the bottom of the capsule; pour the whole contents on to an iron plate, and when cold the mass will leave the iron. Put cake and capsule into a basin, and add water to dissolve the cyanate and excess of cyanide; carefully decant, and when sufficiently washed free from these salts add hydrochloric acid. The metal will dissolve, and after solution pour the whole and wash the capsule into a beaker; add metallic zinc until the last piece ceases to show a tin precipitate. Break up the sponge with a rod, dilute, and when settled carefully pour off the zinc chloride and wash until the tin is pure; again dissolve in hydrochloric acid, dilute, and estimate tin by a standard solution of potassium bichromate, using

potassium iodide and starch-water. The metals may be reduced by a stream of dry hydrogen, but with comparatively little advantage. Little more than an hour is required for an estimation.

Mr. A. E. Arnold finds that by treating cassiterite, in a state of fine division, with a rather brisk current of hydrogen at a moderate red heat, it is completely reduced to metallic tin. If a gramme of substance is taken, about two hours' exposure will suffice. This is demonstrated by the following figures: the numbers under 'Found' represent the loss of oxygen estimated by re-weighing the boats after ignition in hydrogen; under 'Calculated' is the theoretical amount of oxygen present in the tin dioxide found in the sample:—

Tin oxide present	Oxygen Loss	
	Calculated	Found
I. 88.89 per cent.	18.66	18.30
II. 64.48 „	18.76	18.69

The tin present may be deduced with tolerable accuracy from the loss of oxygen incurred in the reduction. The above figures were not determined with this object, and are only cited in want of more exact estimations.

The reduced tin may be caused to act upon iron perchloride in a flask fitted with a small valve, and the resulting iron protochloride can be titrated with permanganate or with bichromate. It is preferable, if a complete analysis of the mineral is required, to treat the substance beforehand with hydrochloric acid or aqua regia to remove the soluble gangue. This may consist of volatile sulphides, iron and bismuth oxides, arsenic acid, and copper and iron sulphides, which interfere with the volumetric estimation. The insoluble matter, consisting principally of silica and tin dioxide, is filtered and weighed. It is easily transferred from the platinum crucible to a small porcelain boat, in which it is reduced. Six or eight boats at a time are conveniently ignited in a long glass tube bound with copper foil.

The hydrogen is freed from all traces of sulphur and arsenic by silver nitrate and soda-lime, and well dried. If arsenic acid is present arsenious acid sublimes in the tube, and reveals itself by its crystallisation; but some arsenic remains with the tin.

The contents of the boats, after cooling in hydrogen, are dissolved either in iron perchloride, for titration, or by hydrochloric acid and potassium chlorate, for the subsequent precipitation of the tin as sulphide or hydrate.

Ten or twelve volumetric estimations of tin may thus be made in the course of 12 hours.

Separation of Tin from Antimony.

Mr. F. Wigglesworth Clarke has found that both tin sulphides, if moist and freshly precipitated, are readily decomposed by moderately long boiling with an excess of oxalic acid, sulphuretted hydrogen being

given off. The monosulphide is converted into the insoluble, crystalline, stannous oxalate, while the yellow disulphide is completely dissolved. The commercial 'Mosaic gold,' however, seems to be unacted upon by the reagent. In presence of an excess of oxalic acid, tin cannot be precipitated by sulphuretted hydrogen.

The antimony sulphide behaves in a somewhat different manner. Although, upon long boiling with oxalic acid, considerable quantities of the metal are taken into solution, yet every trace of it may be reprecipitated by sulphuretted hydrogen.

By taking advantage of the solubility of the tin sulphides in oxalic acid, this metal may be separated almost perfectly from antimony. To the solution containing the metals (this solution being prepared in the usual manner for the precipitation of the sulphides) add oxalic acid, in the proportion of about 20 grammes of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about 20 minutes. No precipitate appears at first; but, as soon as the liquid is saturated with the gas, the antimony sulphide begins to fall, and, in a very few moments, is completely thrown down. Then, as usual, the whole should be allowed to stand about half an hour in a warm place before filtering. Every trace of antimony is precipitated, so that in the filtrate from the sulphide nothing can be discovered by Marsh's test, nor can any antimony-stain be produced with zinc upon platinum.

The antimony always carries down a minute trace of tin with it; this trace, however, if the operation has been carefully performed, can scarcely be detected, and generally may be ignored with safety. If, however, the greatest accuracy is desired, it may be well to redissolve the antimony sulphide in an alkaline sulphide, decompose the solution with an excess of oxalic acid, boil with a little strong sulphuretted hydrogen water, filter, and add the filtrate to the tin solution previously obtained.

Since the presence of oxalic acid interferes somewhat with the complete precipitation of tin by ordinary methods, some precautions are needed in the estimation of that metal after the separation. It can be thrown down as follows:—The solution, after being rendered slightly alkaline with ammonia, is mixed with enough ammonium sulphide to redissolve the precipitate at first formed; an excess of acetic acid is added, and the whole allowed to rest several hours in a warm place. Acetic acid must be used, for stronger acids would be liable to set free some of the oxalic acid to redissolve the tin. The precipitate, which at first varies from white to pale yellow, rapidly darkens in colour, and seemingly consists of a mixture of tin oxide and sulphide. It should be washed with a solution of ammonium nitrate, and, after ignition, is weighed as tin binoxide.

Mr. Clarke has also made a few experiments upon indirectly

estimating the proportions of tin and antimony in alloys of the two metals. He oxidises a weighed quantity of the alloy with nitric acid in a porcelain crucible, heats the resulting oxides with ammonium nitrate, and then (regarding the tin as converted into binoxide, and the antimony into antimonious acid) calculates the proportions of the metals from the increase in weight. This method, although by no means giving accurate results, serves very well for rough approximate estimations. It is here cited simply as an easy and convenient process for obtaining a close idea of the constitution of any alloy composed of the two metals. Possibly the method might be so modified as to give accurate estimations.

The following process of separating tin from antimony has given very accurate results:—Thoroughly oxidise the metallic alloy by means of strong nitric acid, evaporate the mass to dryness, and gently heat it. Then fuse it in a silver dish with a large excess of caustic soda. After cooling dissolve in a minimum quantity of water, and then add one-third of its volume of strong alcohol. This precipitates sodium antimoniate, whilst sodium stannate remains in solution. Filter and wash, first with dilute, then with strong alcohol. Next dry the precipitated sodium antimoniate, and fuse it in a porcelain crucible, with an excess of potassium cyanide. The antimony is reduced, and collects in a metallic button at the bottom of the crucible. The solution containing sodium stannate is boiled to expel alcohol, diluted, acidulated with dilute sulphuric acid, and saturated with sulphuretted hydrogen gas. The precipitated tin sulphide is then oxidised to tin binoxide, and this then reduced to the metallic state by fusion with potassium cyanide, as described on page 404.

Detection of Tin in Presence of Antimony.

Mr. M. M. P. Muir warms the precipitated sulphides of the arsenic group with concentrated hydrochloric acid; the insoluble portion is washed and tested for arsenic by Bunsen's film test. The solution is somewhat diluted; about three-fourths of it is boiled for at least 10 minutes with copper turnings (which must of course be free from tin), poured off from the copper, and tested for stannous chloride by adding mercuric chloride. The remaining smaller portion of the solution is poured on to a piece of platinum surrounded by a piece of zinc-foil. If the platinum become covered with a black deposit it is removed and examined in the ordinary way.

Volumetric Estimation of Antimony in Presence of Tin.

Mr. E. F. Herroun proposes the following method, applicable to Britannia metal, type metal, &c. The alloy in a state of fine division is dissolved in strong hydrochloric acid with the aid of heat, and with frequent additions of small quantities of potassium chlorate. After the whole of the metal is dissolved a small piece of potassium chlorate

is added to ensure the conversion of the antimonious chloride into antimonic chloride, and the solution gently boiled until all the chlorine oxides have been expelled. The solution is then allowed to cool, and a slight excess of a strong solution of potassium iodide added. The free iodine is then estimated by means of a standard solution of sodium thiosulphate.

Since 122 parts of antimony liberate 254 parts of iodine, the amount of iodine found multiplied by 0.48031 will give the amount of antimony present.

If iron or other metal whose perchloride is capable of liberating iodine be present in the alloy the tin and antimony may be obtained as oxides by treating the alloy with nitric acid and evaporating, and, after being well washed, may be boiled in strong hydrochloric acid, and the antimony estimated as above.

Separation of Tin from Bismuth.

To the strong hydrochloric solution of the two metals add a large excess of water. This produces an insoluble precipitate of bismuth oxychloride, which may either be dried, and weighed in that state, or fused to a metallic button under potassium cyanide. The tin will remain in solution.

Separation of Tin from Thallium.

When these two metals occur together in a liquid, they may be separated by adding an excess of ammonium sulphide to the alkaline solution. Thallium sulphide will be precipitated, whilst the tin will remain in solution.

Sulphuretted hydrogen passed through an acid solution containing tin and thallium precipitates the tin, but a little thallium is carried down by the tin sulphide.

Quick Process for the Estimation of Lead in Samples of Tin.

M. Roux proposes the following method:—The alloy is laminated, and 2.5 grammes are dissolved in 15 c.c. nitric acid in a flask marked at 250 c.c. The nitrous vapours are expelled by boiling, and after 40 c.c. of a saturated solution of sodium acetate have been added, it is diluted to 250 c.c., and the stannic acid is allowed to deposit. Of the clear supernatant liquid 100 c.c. are taken, corresponding to 1 gramme alloy, and there are introduced into it 10 c.c. of a titrated solution of potassium bichromate containing 7.13 grammes per litre, and of which 1 c.c. throws down 1 centigramme of lead. After the lead chromate has been deposited, 10 c.c. more are added, and so on till the liquid is coloured yellow by the excess of bichromate. The liquid is filtered, the precipitate washed, and the excess of bichromate estimated by means of a solution containing, per litre 57 grammes

of double iron and ammonium sulphate and 25 grammes sulphuric acid. This liquid is preserved in a sort of washing-bottle under a layer of petroleum or benzol. Nevertheless its standard must be frequently verified. To ascertain the excess of bichromate employed spots are made upon a white porcelain plate with a very dilute solution of potassium ferricyanide preserved in a black bottle. As long as there is not an excess of ferrous oxide in the liquid, the spots retain their reddish-yellow colour, but as soon as the bichromate is completely reduced the spots take a tint, green at first and then blue. If lead is precipitated in presence of stannic acid, there occurs an error of about 2 per cent., in consequence of the potassium bichromate mechanically entangled in the precipitate. If the liquid does not appear red after titration with iron, enough sodium acetate has not been added.

Separation of Tin from Lead.

To detect and separate small quantities of lead in the presence of a great excess of tin, treat a small quantity of the metal with an excess of nitric acid, diluted with 3 times its weight of water, boil the mixture, filter, and then drop into the solution a crystal of potassium iodide. If only $\frac{1}{10000}$ part of lead is present, a yellow precipitate is formed, which does not disappear on adding an excess of ammonia.

Separation of Tin from Copper (Analysis of Gun and Bell Metals, containing, besides, traces of Lead, Zinc, and Iron).

The following process has been employed for some years in H. Sainte-Claire Deville's laboratory at the École Normale:—Dissolve about 5 grammes of the alloy in strong nitric acid contained in a flask provided with a funnel in the neck to prevent loss by spitting. When quite dissolved boil the strong solution for about 20 minutes; dilute with 2 or 3 times its bulk of water, and boil again for the same time. Separate the insoluble tin oxide by decantation or filtration, and weigh after calcining it. (The tin oxide is sometimes rose-coloured, owing to the presence of minute traces of gold; this may be disregarded.) The nitric acid solution freed from the tin is evaporated on a small platinum or porcelain dish, and the residue is calcined at a dull-red heat. In this manner a mixture of oxides is obtained in sufficient quantity to suffice for at least two analyses.

About 2 grammes of the finely pulverised oxides are placed in a small platinum or porcelain boat, and thence introduced into a small glass tube closed with a good cork suitable for weighing. The boat, the tube, and the cork having been previously weighed, the weight of the oxides is obtained after they have been heated to dull redness in the apparatus, through which a current of dry air circulates. After having weighed the whole the current of air is replaced by dry hydrogen, and

the tube is heated over a lamp until the contents cease to lose weight. It then contains unreduced zinc oxide, together with copper, lead, and iron in the metallic state; the colour of the product shows the operator when the experiment is concluded). On weighing again, the loss of weight indicates with great accuracy the amount of oxygen contained in the oxides of these three metals.

If the iron and lead are present in inappreciable quantities, by multiplying this loss by 5 will be given very nearly the weight of copper present, and, in consequence, the composition of the alloy itself. In an approximate analysis of gun-metal the operation will, therefore, be terminated. If, however, a complete analysis is required, proceed as follows:—

Prepare a roughly standard solution of sulphuric acid (which has been distilled from ammonium sulphate). Of this solution, in 200 or 300 c.c. of water, take a sufficient quantity to dissolve about double the amount of the mixed iron and zinc which are supposed to be present.¹ Boil the acid liquid to completely expel the air, and cool it in a flask, which should be almost full and well corked. Then introduce into it the platinum or porcelain boat containing the zinc oxide and the reduced metals. The zinc oxide quickly dissolves, together with the iron, the solution of which is facilitated by the presence of the metallic copper. The copper and lead remain. The flask must be frequently shaken, so as to diffuse these metals throughout the liquid, and the whole is allowed to stand for some hours; the clear liquid is then carefully decanted and the metals washed with boiling water. During this operation a trace of copper or lead may, perhaps, get into solution in the form of sulphate, through the action of the air, or be carried over mechanically. This may be ascertained by adding to the solution a few drops of a clear solution of sulphuretted hydrogen and heating. If brown flocks are deposited, separate them by decantation and add them to the metals.

The solution only contains the zinc and iron sulphates; evaporate to dryness, heat the sulphates to a temperature of about 400° C., and weigh. If no iron is present, the amount of zinc present may be calculated at once. This method of estimating zinc is very accurate. If iron is present it may be separated from the zinc by methods given on page 215. The author, however, recommends the following process:—

Calcine the sulphates in a muffle to reduce them to the state of oxides. Weigh and then moisten them with strong nitric acid until the zinc has all dissolved; evaporate to dryness and heat gently on a sand-bath until nitrous vapours cease to appear; the iron nitrate will then be decomposed. Boil out with solution of ammonium nitrate containing a few drops of ammonia, which will only dissolve the zinc. Wash by decantation, and weigh the residual iron oxide, whose weight

¹ It is a good plan always to weigh the reagents used in analysis, or, at all events, to ascertain approximately the quantities taken.

of double iron and ammonium sulphate and 25 grammes sulphuric acid. This liquid is preserved in a sort of washing-bottle under a layer of petroleum or benzol. Nevertheless its standard must be frequently verified. To ascertain the excess of bichromate employed spots are made upon a white porcelain plate with a very dilute solution of potassium ferrieyanide preserved in a black bottle. As long as there is not an excess of ferrous oxide in the liquid, the spots retain their reddish-yellow colour, but as soon as the bichromate is completely reduced the spots take a tint, green at first and then blue. If lead is precipitated in presence of stannic acid, there occurs an error of about 2 per cent., in consequence of the potassium bichromate mechanically entangled in the precipitate. If the liquid does not appear red after titration with iron, enough sodium acetate has not been added.

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Separation of Tin from Copper (Analysis of Gun and Bell Metals, containing, besides, traces of Lead, Zinc, and Iron).

The following process has been employed for some years in H. Sainte-Claire Deville's laboratory at the École Normale:—Dissolve about 5 grammes of the alloy in strong nitric acid contained in a flask provided with a funnel in the neck to prevent loss by spiriting. When quite dissolved boil the strong solution for about 20 minutes; dilute with 2 or 3 times its bulk of water, and boil again for the same time. Separate the insoluble tin oxide by decantation or filtration, and weigh after calcining it. (The tin oxide is sometimes rose-coloured, owing to the presence of minute traces of gold; this may be disregarded.) The nitric acid solution freed from the tin is evaporated on a small platinum or porcelain dish, and the residue is calcined at a dull-red heat. In this manner a mixture of oxides is obtained in sufficient quantity to suffice for at least two analyses.

About 2 grammes of the finely pulverised oxides are placed in a small platinum or porcelain boat, and thence introduced into a small glass tube closed with a good cork suitable for weighing. The boat, the tube, and the cork having been previously weighed, the weight of the oxides is obtained after they have been heated to dull redness in the apparatus, through which a current of dry air circulates. After having weighed the whole the current of air is replaced by dry hydrogen, and

the tube is heated over a lamp until the contents cease to lose weight. It then contains unreduced zinc oxide, together with copper, lead, and iron in the metallic state; the colour of the product shows the operator when the experiment is concluded). On weighing again, the loss of weight indicates with great accuracy the amount of oxygen contained in the oxides of these three metals.

If the iron and lead are present in inappreciable quantities, by multiplying this loss by 5 will be given very nearly the weight of copper present, and, in consequence, the composition of the alloy itself. In an approximate analysis of gun-metal the operation will, therefore, be terminated. If, however, a complete analysis is required, proceed as follows:—

Prepare a roughly standard solution of sulphuric acid (which has been distilled from ammonium sulphate). Of this solution, in 200 or 300 c.c. of water, take a sufficient quantity to dissolve about double the amount of the mixed iron and zinc which are supposed to be present.¹ Boil the acid liquid to completely expel the air, and cool it in a flask, which should be almost full and well corked. Then introduce into it the platinum or porcelain boat containing the zinc oxide and the reduced metals. The zinc oxide quickly dissolves, together with the iron, the solution of which is facilitated by the presence of the metallic copper. The copper and lead remain. The flask must be frequently shaken, so as to diffuse these metals throughout the liquid, and the whole is allowed to stand for some hours; the clear liquid is then carefully decanted and the metals washed with boiling water. During this operation a trace of copper or lead may, perhaps, get into solution in the form of sulphate, through the action of the air, or be carried over mechanically. This may be ascertained by adding to the solution a few drops of a clear solution of sulphuretted hydrogen and heating. If brown flocks are deposited, separate them by decantation and add them to the metals.

The solution only contains the zinc and iron sulphates; evaporate to dryness, heat the sulphates to a temperature of about 400° C., and weigh. If no iron is present, the amount of zinc present may be calculated at once. This method of estimating zinc is very accurate. If iron is present it may be separated from the zinc by methods given on page 215. The author, however, recommends the following process:—

Calcine the sulphates in a muffle to reduce them to the state of oxides. Weigh and then moisten them with strong nitric acid until the zinc has all dissolved; evaporate to dryness and heat gently on a sand-bath until nitrous vapours cease to appear; the iron nitrate will then be decomposed. Boil out with solution of ammonium nitrate containing a few drops of ammonia, which will only dissolve the zinc. Wash by decantation, and weigh the residual iron oxide, whose weight

¹ It is a good plan always to weigh the reagents used in analysis, or, at all events, to ascertain approximately the quantities taken.

will at the same time enable the weight of the zinc oxide associated with it to be calculated. The zinc and ammonium nitrates may, moreover, be evaporated to dryness and decomposed by heat, when the residual zinc oxide can be weighed, but this is an unnecessary operation.

The mixture of copper and lead (to which has been added the trace of sulphides which may have been separated from the sulphuric solution of the iron and zinc) may be separated by the process given at page 215. Or the following process, recommended by Deville, may be employed:—Dissolve the mixture in sulphuric acid containing a little nitric acid; the solution, more or less turbid from the presence of lead sulphate, is evaporated to dryness on a sand-bath and heated to about 400° C. Weigh the mixed sulphates and extract the copper sulphate with water. Lead sulphate will remain, the weight of which subtracted from the total weight of the sulphates gives the copper sulphate.

Separation of Tin from Tungsten.

Stannic and tungstic acids may be separated by igniting the mixture with sal-ammoniac, when the tin will be completely volatilised in the form of chloride, whilst the tungstic acid remains unchanged. As the conversion of stannic acid into volatile tin chloride requires a long time, the treatment of the mixture, with 6 or 8 times its weight of sal-ammoniac, must be repeated several times, until no further loss of weight is observed. Great care must be taken that the outside of the porcelain crucible and cover does not become covered with stannic acid, which may be formed afresh from the chloride and atmospheric moisture. Hence the smaller crucible should be placed in a larger one similarly covered, and heated to a tolerably high temperature. The residue of tungstic acid becomes coloured green, then blackish. When heated in the air it assumes its usual yellow colour, and its weight is then constant.

Another satisfactory method of separating tin from tungsten has been described by Mr. J. H. Talbott.

The method is based on the fact that tin oxide is reduced by potassium cyanide with great facility; while tungstic acid undergoes no reduction, even when heated with the cyanide at a high temperature. The tin and tungsten oxides are to be heated in a porcelain crucible with 8 or 4 times their weight of commercial potassium cyanide previously fused, pulverised, and thoroughly mixed with the two oxides. The mass is kept fused for a short time, when the tin separates in the form of metallic globules, while the tungstic acid unites with the alkali of the potassium cyanate and carbonate present. After cooling, the mass is to be treated with hot water, which dissolves the alkaline tungstate and other salts and leaves the tin as metal; this is to be separated by filtration, washed, dried, and weighed as tin oxide, after oxidation in the crucible with nitric acid. The tungstic acid may be estimated by

difference, or be precipitated by mercury protonitrate, after boiling the solution with nitric acid to decompose the excess of potassium cyanide present, and then redissolving the precipitated tungstic acid by means of an alkali.

Commercial Analysis of Tin Ware.

The chief drawback to the analytical processes used in investigating the composition either of utensils of block tin or of thin layers of tin covering other metals, such as copper and iron, is the excessive weight of the metal to be operated on recommended in special treatises on the subject.

The following process of analysis, devised by MM. Millon and Morin, has been found to be free from the objections attaching to the ordinary method of analysis with nitric acid.

In a small flask of from 80 to 100 c.c. capacity, furnished with a disengaging-tube, put about $1\frac{1}{2}$ gramme of the tin, taking care to reduce the metal to fine grains, if it be not already divided by scraping; nearly fill the flask with pure fuming hydrochloric acid; adapt to the disengaging-tube a bulb tube containing a solution of gold chloride, and supplement this apparatus with another bent tube plunged into mercury.

The reaction commences in the cold, with a slight effervescence, goes on spontaneously, and ceases in about 24 hours. The presence of antimony or arsenic greatly favours the gaseous disengagement; scraped tin is usually more easily attacked than granulated tin.

The evolved gas traversing the bulb tube is composed of a mixture of hydrogen and arseniuretted hydrogen; all the arsenic escapes in the latter form, unmixed with antimoniuretted hydrogen; it remains in the gold chloride, where the arsenic acid is to be sought for and estimated in the usual manner.

When the proportion of arsenic is considerable, the gaseous disengagement becomes so rapid that one bulb tube is insufficient to arrest the arseniuretted hydrogen; but this never happens in the analysis of tinware used for domestic purposes; traces only of arsenic are found in this tin, at the most a few thousandths. However, if in an exceptional instance the amount of arsenic exceeds these limits, the difficulty is overcome by operating on a much less weight of alloy, and using hydrochloric acid, diluted with about a fourth of its volume of water.

Antimony and tin alloy resists fuming hydrochloric acid when the antimony is in the proportion of 25 to 80 per cent. The alloy must then be melted with a given quantity of fine tin. To facilitate the action of the hydrochloric acid, nitric acid is added to it drop by drop; the antimony is then precipitated by tin, in presence of a large excess of hydrochloric acid.

When the action of the hydrochloric acid ceases, and no more

gaseous bubbles are given off, a more or less abundant black powder is seen at the bottom of the flask, containing all the antimony existing in the tin. This antimony is free from arsenic, but retains the copper. There should also be found the bismuth, which is frequently mentioned by analysts, but which the authors have never once been able to detect.

The copper remains in the black powder, except when it exists in larger proportion than 20 per cent. in the alloy.

The black powder also occasionally contains traces of iron, but this is so slight in quantity that its presence may pass unnoticed.

The supernatant acid liquid is decanted, the black powder washed with distilled water, and the acid liquids mixed. After being well washed the powder is attacked by weak nitric acid (with concentrated acid the reaction is so energetic as sometimes to ignite the powder). The excess of nitric acid is got rid of by boiling, and the residue, containing antimony and copper, is evaporated to dryness and slightly calcined over a lamp.

The residue is dissolved in water acidulated with nitric acid, which dissolves the copper oxide, but takes with it a little antimony. If calcined in too hot a flame, the copper oxide cannot be separated from the antimonious acid. Any bismuth existing in the alloy would be found with the copper in the nitric solution.

This process for separating antimony and copper is not quite perfect. If greater accuracy is desired, it may be effected by pouring pure fuming hydrochloric acid on the black powder, then boiling, and afterwards adding carefully, drop by drop, a saturated solution of potassium chlorate; the powder dissolves, and the copper and antimony are then separated by the addition of an excess of potassium sulphide, in which the antimony sulphide alone dissolves, the copper sulphide remaining insoluble.

The hydrochloric liquid decanted from the black powder and mixed with the washing water is now to be examined. The liquid holds tin in solution, together with lead, iron, and zinc, and in it we must also look for the exceptional presence of cadmium, cobalt, and nickel.

The hydrochloric liquid is diluted with several times its volume of water, and a current of sulphuretted hydrogen is directed through it; the lead and tin are precipitated, the iron and zinc remaining in solution. Were the other metals present, the cadmium would be precipitated with the lead and tin, while the nickel and cobalt would be found with the iron and zinc. But the three exceptional metals, cadmium, nickel, and cobalt, need scarcely be taken into account, as their presence has only once been detected, and then in insignificant proportion.

The lead and tin precipitated as sulphides are shaken up with ammonium sulphide in excess at a moderate temperature; the lead sulphide remains insoluble; it is washed, oxidised by nitric acid, and

weighed in the state of sulphate. The tin sulphide, completely dissolved in the ammonium sulphide, is precipitated by weak hydrochloric acid, then collected, dried, calcined in the air, moistened with nitric acid, and reheated before being weighed.

After the separation of lead and tin, iron and zinc are searched for in the liquid, through which a current of sulphuretted hydrogen has been passed. This liquid is evaporated to dryness and dissolved in hydrochloric acid; the iron is peroxidised by a little nitric acid, again evaporated, redissolved by hydrochloric acid, and to the hot liquid ammonia in excess is added to precipitate the iron oxide. The zinc in the filtered liquid now remains to be precipitated. The solution is brought near the boiling-point, and sodium carbonate in excess is added drop by drop, which precipitates all the zinc. The iron and zinc in the solution may also be separated by methods described at page 215.

ARSENIC.

Purification of Metallic Arsenic.

In order to restore to this metal its bright aspect, and to remove any slight coat of suboxide which may adhere to it, the metallic arsenic should be boiled for a few minutes in a moderately strong solution of potassium bichromate, slightly acidified with sulphuric acid. The metal is next washed with water, and then with alcohol or ether, and lastly placed in a small tube closed at one end, and sealed immediately after.

Detection of Arsenic by Marsh's Test.

When distilled magnesium, as now commonly met with in commerce, is introduced into a solution containing arsenic acidulated with sulphuric or hydrochloric acid, the arsenic is entirely separated in the form of arseniuretted hydrogen. Magnesium possesses great advantages over zinc for toxicological purposes. It is now met with in commerce almost absolutely pure, and the original materials and processes of its manufacture quite remove the poisonous metals most dreaded by chemists—copper, lead, mercury, arsenic, antimony, &c. It is met with in the form of long slight ribbons, well fitted for delicate laboratory experiments. It keeps well in ordinary air. Its low equivalent displaces the ordinary poisonous metals by relatively small proportions of the precipitating metal, and the perfectly harmless character of the magnesium salts, added to the fact that it is a normal constituent of the animal body, render its introduction into suspected fluids a matter of no consequence.

There is one precaution which must be taken in using magnesium in Marsh's apparatus. Magnesium which contains silicium gives off on contact with acids siliciuretted hydrogen, which decomposes at a dull red heat like arseniuretted and antimoniuiretted hydrogen, leaving

a dark brown deposit. The formation of this deposit might give rise to an error. A few words will answer this objection.

1. The magnesium which is now manufactured gives no foreign deposit in Marsh's apparatus; no sample of magnesium ribbon (as it is made for burning) yet tested has given either rings or spots. The hydrogen it gives off has always appeared remarkably pure and inodorous; its flame is hardly visible.

2. Marsh's apparatus fed by magnesium is tested under precisely the same conditions as when fed by zinc. The suspected liquids are only introduced into the apparatus after the preliminary verification of the gas-producing agents.

3. The deposit of silicium left in the red-hot tube by the passage of the hydrogen accidentally charged with siliciuretted hydrogen is, moreover, clearly distinguishable from the deposits of arsenic and antimony. These last two disappear immediately on contact with a drop of nitric acid or aqua regia; the ring and spot of arsenic disappear suddenly when touched with a dilute solution of a hypochlorite. These three tests have no effect on the deposits of silicium produced in the tube of the apparatus.

If the suspected liquids contain no trace of arsenic or antimony, they may contain other poisonous metals, such as copper, lead, mercury, zinc, &c. In this case the metals are found as flakes, powder, or sponge, either at the bottom of the flask of the apparatus or on the surface of the plates of magnesium. To render the precipitation complete, the liquids must be kept in a proper state of acidity, and the experiment prolonged till the new plates of magnesium introduced into the liquid dissolve, whilst retaining their metallic brilliancy. To ascertain the end of the operation, it is well to take out at first a small portion of the liquid of the flask, to put it into a small test-tube, and to introduce a well-cleaned ribbon of magnesium. However it may be, it is always necessary to leave in the flask a small excess of magnesium before pouring the liquid on a filter. All that is in suspension—corroded plates of magnesium, powder, flakes, or metallic sponge—is washed on the filter until the washings show no acid reaction; the filtered liquids should not precipitate on the addition of hydrosulphuric acid. The filter being dried, collect the deposit it contains, and analyse it in the ordinary way, to ascertain the metals precipitated by the magnesium.

As an improvement on this process the matter containing the arsenious or arsenic acid is introduced into a Marsh's apparatus and mixed with a concentrated solution of caustic potash and a little aluminium foil. Arseniuretted hydrogen is disengaged on applying heat. Antimoniuretted hydrogen is not formed.

Another modification of the Marsh process is as follows:—The substance in question is mixed with a little water, or its solution is poured into a small beaker, and a piece of sodium amalgam as large

as a grain of wheat is introduced. The beaker is then covered as rapidly as possible with a piece of white filter-paper or a porcelain lid, previously moistened with a weak feebly acid solution of silver nitrate. The presence of arsenic is indicated by a blackening of the paper or of the porcelain. As antimony hydride is not given off, or in mere traces—from strongly alkaline liquids, the solution should be rendered distinctly alkaline—in this manner the confusion of antimony and arsenic is rendered improbable, though not quite excluded. Organic matter does not interfere.

Improvement in Marsh's Apparatus.—Everyone who has experimented with an extemporised Marsh's apparatus has found that, after the gas has burned a short time, the glass tube has become fused and the aperture closed. This may be prevented by platinising the extremity of the tube. Draw out the tube, file it to make it a little rough, and then dip it into a strong solution of platinum bichloride, so as to take up a drop or so. Then carefully heat the point until it acquires a beautiful metallic lustre. By repeating this four or five times a good coating of platinum is obtained both outside and inside.

For the Detection of Arsenic in either Organic or Inorganic Matter.

MM. Mayençon and Bergeret place pure zinc in a small flask containing distilled water acidulated with pure sulphuric acid, and close its neck imperfectly with cotton-wool, to prevent drops of the liquid being thrown upon the test-paper, which is simply tissue paper moistened with a solution of mercury bichloride, and used before it dries. If this paper is exposed to pure hydrogen no change appears; but if any arsenical compound is placed in the flask, a lemon-yellow spot appears, which gradually deepens to a pale yellowish brown. Antimoniuretted hydrogen produces a brownish-grey spot, quite distinct from the arsenical colouration. The reaction is exceedingly delicate.

Detection of Arsenic in the Colours of Paper Hangings.

Prof. Hager recommends the following method:—A little of the paper is steeped in a concentrated solution of sodium nitrate obtained by dissolving this salt in a mixture of equal parts of alcohol and water, and letting it dry. Then the paper is burnt upon a porcelain saucer. The combustion generally takes place quietly and without a flame. Water is poured upon the ashes, potash in excess is added, and the whole boiled and filtered. Dilute sulphuric acid is added, and then potassium permanganate, which is added gently as long as the red colour disappears, and gives place to a yellow under the influence of heat. If the liquid becomes turbid it is filtered anew. It is let cool, and more dilute sulphuric acid added, and a small plate of pure zinc. This should be done in a flask, which is then stoppered

with a cork having two slits. In one of these is placed a slip of paper steeped in a solution of silver nitrate; in the other, a piece of parchment moistened with lead acetate. If arsenic is present, the silver paper blackens. The lead paper only serves to detect sulphuretted hydrogen.

Reinsch's Test for Arsenic.

This process consists, as is well known, in extracting arsenic from its hydrochloric solution, by means of metallic copper. The black deposit which results is usually regarded as pure arsenic. M. Lippert has shown that this deposit contains only 82 per cent. of arsenic, the remainder being copper. This is a true alloy, of a definite and constant composition, having the formula Cu_3As .

When heated in a hydrogen current, this black powder loses a little arsenic, and is transformed into a white silvery alloy, oxidising slightly in the air, agreeing in its composition, Cu_3As , with *Domeykite*, a mineral found at Copiabo. The great sensitiveness of Reinsch's process arises, then, from the large proportion of copper alloyed with the deposited arsenic. It must, however, be remembered that all the arsenic will not be volatilised by heating in a hydrogen current, and that at least half will remain in the deposit. (See also Separation of Arsenic from Copper.)

To distinguish the arsenical deposit obtained in Reinsch's process from one formed by a mercury salt, Mr. James St. Clair Gray first washes one of the copper slips coated in the ordinary manner by Reinsch's process in pure distilled water, and then thoroughly dries it; when thus prepared it is rubbed with a flattened bead of pure gold, or, should this not be at hand, a flat signet-ring will suffice. The result, if the coating be mercurial, is that a portion of the mercury, whose affinity for gold is greater than for copper, is transferred from the copper to the gold, appearing on its surface as a clear white, shining, metallic crust, this being more conspicuous the more highly coloured the surrounding gold is. This stain is at once removed by pure strong nitric acid. This is of itself perfectly conclusive of the presence of mercury in the metallic coating or deposit on the copper, and is equally applicable should there exist in that deposit a combination of mercury with any or all of the other three metals which yield by Reinsch's process a metallic deposit on copper-foil.

Identification of Arsenious Acid by Crystallisation.

By allowing the crystals of arsenious acid to form very gradually by slow cooling, they can be obtained very large and perfect. The following mode of forming them is the one recommended by Dr. F. W. Griffin:—Drive the substance entirely off the lower half of the tube, which is made very hot by waving it about in the flame. Then revaporise the sublimate, holding the tube (which should be closed by a loosely-fitting cork) as upright as possible. The dense vapour

sinks to the bottom, and will give large and regular crystals as the glass slowly cools. These crystals glitter in the sun like diamonds, and exhibit the same play of colours; they are from the $\frac{1}{150}$ to the $\frac{1}{100}$ of an inch in diameter, and under a 1-inch objective form specimens for the micro-crystallographer. Here and there we find octahedra absolutely perfect, but they are more frequently truncated, all the angles, however, being beautifully sharp. The majority are transparent, but some are only translucent, or even opaque. By reflected light (using a bull's-eye condenser) they appear, in consequence of their adamantine lustre, like diamonds lying in high relief on a black ground; but their complete shape is most strikingly displayed by a combination of strong reflected and feebler transmitted rays of various degrees of obliquity. A tube of $\frac{1}{2}$ inch in diameter, under a 1-inch objective, presents nearly the entire field in focus, and the perfect crystals appear from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch in diameter.

Estimation of Arsenious Acid in Presence of Arsenic Acid.

M. L. Mayer takes as a point of departure the known property of arsenious acid to reduce ammoniacal solution of silver at a boiling heat, and bases upon it a convenient gravimetric method for the estimation of arsenious acid along with arsenic acid. The common method of precipitating arsenic with magnesia solution as ammonio-magnesium arseniate is not free from sources of error, due to the solubility of the latter compound. The methods of H. Rose and Vohl are tedious and circumstantial. Mayer's method depends upon the following decomposition. If a solution contains in addition to arsenious acid no other substance which reduces the ammoniacal solution of silver at a boiling heat, reduction takes place, and after boiling for half an hour, the reduced silver separates out as a fine powder and is filtered off and weighed. The quantities of silver thus obtained agree exactly with the arsenious acid employed. The reduced silver must be washed with warm ammonia and water containing sal-ammoniac. If a portion of the silver is reduced in the form of a mirror on the sides of the glass, it is dissolved off in nitric acid, precipitated as silver chloride, which is added to the main quantity of the silver; for such small traces of silver chloride are reduced on ignition by the carbon of the filter. In applying this method for the estimation of arsenious acid in presence of arsenic acid, the arsenious acid is estimated by boiling with ammoniacal solution of silver. On the reduction of the silver, the arsenious acid passes into arsenic acid, which is estimated along with the original arsenic acid. The quantity of the latter is found as difference.

Silver Nitrate Test for Arsenic Acid.

Silver arseniate is slightly soluble in an aqueous solution of ammonium nitrate, and readily soluble in both ammonia and dilute nitric acid; it is, therefore, not easy to detect small quantities of arsenic by means of silver nitrate, as usually employed, unless the test be applied with extreme care. Mr. Every has found that the addition either of sodium acetate, ammonium acetate, or Rochelle salt, to a mixed solution of arsenic and nitric acids, is sufficient to ensure the immediate precipitation of silver arseniate when silver ammonio-nitrate is introduced. Instead of the acetates or tartrates, recently precipitated silver carbonate may be employed to neutralise free nitric acid. When present in relatively large quantity, arsenic acid readily precipitates silver from a solution of ammonium nitrate and silver ammonio-nitrate, but the colour of the precipitate is uncertain.

For the recognition of arsenic acid, E. Salkowski dissolves arsenic sulphide in fuming nitric acid, expels the greater part of the acid by evaporation, heats the residue with water holding in suspension calcium or barium carbonate, and filters. The calcium and barium arseniates are sufficiently soluble for the filtrate to give a red precipitate on adding silver nitrate.

Detection of Arsenic in Commercial Hydrochloric Acid.

When arsenious or arsenic acid is dissolved in fuming hydrochloric acid, and a solution of tin protochloride dissolved in hydrochloric acid is added thereto, a brown-coloured, very bulky precipitate is formed, which rapidly settles down. After having been collected on a filter and washed, first with hydrochloric acid and then with water, to remove the acid, and then dried over sulphuric acid *in vacuo*, the precipitate forms a greyish-coloured powder of metallic aspect; this, on being rubbed in an agate mortar, exhibits metallic lustre, and partially volatilises on being heated, while oxide of tin, in the shape of a very light powder, is left. The precipitate consists of from 98.46 to 95.86 per cent. of metallic arsenic, according as arsenious acid, arsenic acid, or ammonium arseniate and magnesium has been employed. The precipitate is never obtained quite free from tin. When the hydrochloric acid employed has a sp. gr. of 1.115, the arsenious or arsenic acid dissolved therein becomes for the most part converted into arsenic chloride; and the reaction, therefore, takes place between that chloride and tin protochloride. When the hydrochloric acid has a sp. gr. of 1.1, the arsenious acid is not converted into arsenic chloride, but is dissolved as arsenious acid. Tin chloride does not act upon combinations of antimony under the same conditions.

In order to eliminate all arsenic from it, crude hydrochloric acid, sp. gr. 1.104, should be treated with a strong solution of tin protochloride in pure hydrochloric acid, left standing for 24 hours, and the

precipitate removed by filtration. The acid is next placed in a retort, the first $\frac{1}{10}$ of the distillate kept separately, and the remainder distilled off to dryness, when that portion will be found absolutely free from arsenic; the first $\frac{1}{10}$ may in some cases retain as much as 0.02 per cent. of arsenic.

Separation of Arsenic.

Emil Fischer finds that arsenic may be very conveniently separated from a given mixture with other metals by distillation with ferrous chloride, and its subsequent estimation effected with solution of iodine. This offers so great advantages that scarcely any of the older methods will be used when the estimation of this element alone is required. If the substance in question is already dissolved, the whole operation may be completed in 4 hours. The process is especially adapted for chemico-legal cases.

Estimation of Arsenic as Magnesium Pyroarsenate.

Dr. F. Reichel places the well-dried precipitate as completely as possible in a watch-glass, moistens the filter with a solution of ammonium nitrate, dries, and burns it, previously cut up into pieces, in a porcelain crucible. When the crucible is cold the contents of the watch-glass are introduced into it, a few drops of nitric acid added so as to saturate the whole precipitate, and the crucible is dried at 100° or heated carefully over a small gas-flame, to prevent spirting. As soon as the watery vapours no longer escape, the crucible is closed, and ignited strongly for 10 minutes.

C. Rammelsberg remarks that if magnesium ammonio-arsenate is dried at 100° to 110° , as commonly recommended, a part of the ammonia escapes. It is best to dry at 120° , and ignite with proper precautions. There is no reduction of arsenic. The volumetric estimation of the arsenic acids—arsenic acid being previously reduced by means of sulphurous acid—by supersaturating with potassium bicarbonate, adding starch paste, and titrating with solution of iodine, is very useful.

Separation of Arsenic from Gallium.

In a strong hydrochloric solution hydrogen sulphide precipitates the arsenic entirely, whilst all the gallium remains in solution. The arsenic sulphide is washed with water acidified with hydrochloric acid, and not with pure water, to prevent the precipitate from passing through the filter.

Volumetric Estimation of Small Quantities of Arsenic and Antimony.

A. Houzeau has observed that the hydrogen compounds of arsenic and antimony are almost entirely and instantaneously absorbed by slightly-acidulated silver nitrate.

On this reaction, an accurate and sensitive process for the indirect estimation of arsenic and antimony according to the quantity of silver precipitated can be based, and also a direct process for the estimation of arsenic according to the proportion of arsenious acid formed.

Indirect Process.—This process is carried on in the following manner:—The substance containing arsenic or antimony, so prepared that it can be reduced by hydrogen, is placed in a Marsh apparatus in which hydrogen is evolved from pure zinc and pure hydrochloric acid. The gas is first conducted through a column of chalk (lumps of chalk put into a tube placed vertically), and next into a titrated solution of neutral silver nitrate, which is then diluted with its own bulk of water, and acidulated with 2 or 3 drops of nitric acid, or, still better, by 0.5 c.c. of acetic acid, so as to prevent the precipitation of a certain quantity of silver arsenite. The silver which remains in solution is estimated by means of a standard solution of common salt.

The estimation of the arsenic may be performed by the direct method, consisting in a chlorometric process with the silver solution which has been used for absorbing the arseniuretted hydrogen. For this purpose the whole of the silver is precipitated by a slight excess of a 8 per cent. sodium chloride solution; the volume of the liquid and precipitate is measured (say 25 or 50 c.c.), and the whole thrown on to a perfectly dry filter, which is not washed. The clear filtered liquid is first measured (say 22 to 40 c.c.), and then poured into a test-glass, and there is added to it 1 or 2 c.c. of perfectly pure and colourless hydrochloric acid. The quantity of arsenious acid is next estimated by means of a titrated solution of potassium permanganate.

The methods simultaneously applied may be used to estimate with precision a mixture of arsenical and antimonial compounds, and also for the quantitative analysis of arseniuretted hydrogen mixed with antimonuretted hydrogen.

The method is also applicable to the estimation of arsenic and antimony mixed with organic substances, but it is necessary to first destroy these substances.

Although this method is only directly applicable to those antimonial and arsenical compounds which admit of being reduced by nascent hydrogen, such as arsenic and arsenious acids, antimonious acid, &c., the use of this method may be extended to arsenic sulphides and phosphides, after the previous oxidation of these substances by means of hydrochloric acid and potassium chlorate.

This process of oxidation will always have to be resorted to when arsenic or antimony is to be detected in a combination of unknown composition, because sulphurous, sulphhydric, and phosphuretted hydrogen compounds will affect the silver solution in the same manner as arseniuretted and antimonuretted hydrogen. Pure hydrogen does not reduce the silver nitrate solution.

Estimation of Arsenic in Arsenic Tersulphide.

To estimate the arsenic contained in arsenic tersulphide—an operation often necessary for the estimation of arsenic—M. Graebe uses a standard solution of iodine, as in the estimation of arsenious acid. Suspend the arsenic sulphide in water, add some sodium carbonate, then a little starch paste, and the standard solution of iodine. It is necessary that the arsenic sulphide should be freed from sulphuretted hydrogen. For every equivalent of arsenic tersulphide converted into arsenic acid, 5 equivalents of iodine are decolourised by conversion into hydriodic acid, and 8 equivalents of sulphur are precipitated.

Estimation of Arsenic in Arsenic Pentasulphide.

A solution of arsenic pentasulphide in ammonium sulphide instantly yields a precipitate of magnesium ammonio-arsenate by a solution of magnesia. Lenssen states that the tin and antimony sulphides are not precipitated under the same conditions. Attempts to found a process of separating arsenic from tin and antimony on this reaction have proved unsuccessful.

Estimation of Arsenic in Ores.

For estimating the amount of arsenic in ores, Mr. Parnell says that the neatest, simplest, and most accurate mode of procedure is to heat the finely-divided sample in a gentle stream of chlorine gas to a temperature of about 200°C ., and to collect the escaping arsenic chloride in chlorine-water. If free from antimony, the liquid may be well boiled, to expel free chlorine, and the arsenic precipitated with sulphuretted hydrogen, and weighed as pentasulphide.

In cases where the arsenic is obtained in the form of arsenio-magnesian phosphate (as in separation of the metal from antimony or copper), the most accurate plan would be to dissolve the precipitate in hydrochloric acid and precipitate the arsenic as pentasulphide. When the amount of arsenic is small, it may be weighed as the double arseniate. The sample should not, however, be dried at a higher temperature than that of an ordinary water-bath—namely, about 95°C . Perfectly accurate results could, no doubt, be obtained by drying the precipitate over sulphuric acid, when it retains its 6 equivalents of water. The only objection is that it would take many days for a filter containing a precipitate to be properly dried by this means.

MM. de Clermont and Frommel proceed thus:—Supposing we have a mixture of arsenic, antimony, and tin, the whole is converted into sulphides by treatment with sulphuretted hydrogen, after having acidulated with hydrochloric acid, adding also tartaric acid if antimony is present. When the mixture is saturated it is allowed to stand in a warm place till the odour of sulphuretted hydrogen is no longer perceptible, and is then thrown upon a filter and washed with

much care, as the least residue of hydrochloric acid would cause a loss of arsenic in the state of chloride. The whole is then transferred into a flask full of water, and heated to a boil. The reaction is more rapid in a retort through which a current of air is passed. If the quantity of arsenic does not exceed 2 decigrammes the distillation of 500 to 600 c.c. of water suffices for the complete dissociation of the sulphides. The residue is then filtered, and the entire quantity of the arsenious acid is found in the filtrate, and estimated by the ordinary methods.

Separation of Arsenic from Tin.

Potassium bisulphite dissolves arsenic sulphide, but does not dissolve tin sulphide. The mixture of the two sulphides, oxidised by nitric acid, is allowed to digest with sulphur and caustic potash till solution is complete (or till the formation of a metallic oxysulphide, which is separated by filtration). The liquid, treated by excess of sulphurous acid, is allowed to rest for some time, and is then evaporated till two-thirds of the water and all the sulphurous acid have gone off. Filter off the tin sulphide, and wash it, not with water, which must not be used here, but with a concentrated solution of sodium chloride. This may be removed from the precipitate by means of a slightly acid solution of ammonium acetate, but the liquor so obtained must not be added to the washing waters charged with salt. The tin sulphide, when dried, may be converted into tin oxide by roasting in contact with air. The arsenic which the liquid contains in the state of arsenious acid may be precipitated by a current of sulphuretted hydrogen.

The arsenic sulphides, even upon very long boiling with oxalic acid, are almost unattacked. Very minute traces of the metal sometimes go into solution, but may be reprecipitated by a bubble or two of sulphuretted hydrogen. Accordingly, the presence even of an enormous excess of oxalic acid does not hinder the precipitation of arsenic as sulphide. Both tin sulphides, if moist and freshly precipitated, are readily decomposed by moderately long boiling with an excess of oxalic acid, sulphuretted hydrogen being given off. To separate the two metals proceed as follows:—To the solution containing arsenic and tin (this solution being prepared in the usual manner for the precipitation of the sulphides) add oxalic acid, in the proportion of about 20 grammes of the reagent for every gramme of tin, taking care to have the whole so concentrated that the acid will crystallise out in the cold. Then heat to boiling, and pass in sulphuretted hydrogen for about 20 minutes. No precipitate appears at first; but, as soon as the liquid is saturated with the gas, arsenic sulphide begins to fall, and, in a very few moments, is completely thrown down. Then, as usual, the whole should be allowed to stand about half an hour in a warm place, before filtering. Every trace of

arsenic is precipitated, so that, in the filtrate from the sulphides, it cannot be discovered by Marsh's test. The precipitated arsenic sulphide is absolutely free from tin.

Solution of Arsenical and Antimonial Compounds.

Rammelsberg's method of separating arsenic and antimony from the metals of the fifth group by fusion with sodium carbonate and sulphur and solution in water, has the drawback that the aqueous solutions contain highly sulphuretted compounds, which, on exposure to the air, deposit incrustations of sulphur, and on decomposition with hydrochloric acid precipitate the arsenic and antimony sulphides mixed with much sulphur, which is very inconvenient in dissolving the arsenic sulphide, or, in converting the antimony sulphide into antimonious acid. By using sodium thiosulphate previously completely dehydrated by cautious fusion in a capsule, this inconvenience is avoided, and the sulphides thrown down from the aqueous solution of the melt are contaminated with but little free sulphur.

Separation of Arsenic from Antimony.

An accurate method of separating these two bodies is founded on the fact that recently precipitated arsenic sulphide is soluble in potassium bisulphide, while antimony sulphide is insoluble. If, for example, we have to analyse commercial grey antimony sulphide, or metallic antimony, it can be done as follows:—Mix the finely pulverised and weighed substance with a little sulphur, and digest in a solution of potassium protosulphide; the mass dissolves, generally leaving a black residue, consisting of a mixture of lead, iron, and copper sulphides, which must be filtered off and examined separately. The liquid is mixed and digested with a large excess of water saturated with sulphurous acid, then heated and kept in ebullition till two-thirds of the water has boiled away and there is no smell of sulphurous acid. Antimony sulphide will be precipitated, and from the filtrate from this the arsenic may be precipitated by a stream of sulphuretted hydrogen gas.

Tartar emetic has sometimes been found to contain arsenic. This impurity may be detected in the following manner:—Two grammes of the suspected tartar emetic are reduced to a fine powder and dissolved in 4 grammes of pure hydrochloric acid (sp. gr. 1.124). The glass vessel wherein this solution is made ought to be narrow, and capable of being well closed, and of sufficient size to contain an additional quantity of at least 30 grammes of hydrochloric acid. A quantity of pure hydrochloric acid should be thoroughly saturated with sulphuretted hydrogen gas, and of this acid at least 80 grammes are added to the solution of the tartar emetic. The glass vessel containing the solution is well corked, and, after having been shaken up, set aside; the turbidity which at first appears soon subsides (if it does not do so,

it is due to the too great saturation of the hydrochloric acid with sulphuretted hydrogen, and should be remedied by the addition of pure hydrochloric acid). If no arsenic is present, the liquid remains colourless; but the slightest trace of arsenic gives rise to a yellow colouration, and soon after to a perfectly perceptible pure yellow precipitate of arsenic sulphide.

Among the many methods for separating arsenic from antimony, the one which is based upon the dissimilar deportment of arseniuretted and antimoniuiretted hydrogen with silver nitrate deserves to be favourably mentioned; the former, yielding arsenious acid, which passes in solution; the latter giving rise to the formation of silver antimonide, which is insoluble in water. The arsenic may be recognised in solution by ammonia, if there be an excess of silver, or by sulphuretted hydrogen, if the silver has been entirely precipitated. By boiling the mixture of silver and silver antimonide, after the arsenious acid has been carefully washed out by boiling water, with tartaric acid, this dissolves the antimony alone, and the solution thus obtained yields at once the characteristic orange-yellow precipitate with sulphuretted hydrogen.

With minute quantities this process proves successful, inasmuch as 5 milligrammes of either metal in the presence of 100 times the amount of the other can be satisfactorily exhibited. In evolving the hydrogen compounds of arsenic and antimony, care must be taken to add as little nitric acid as possible to the hydrochloric acid used in dissolving the sulphides of the metals, since the presence of even moderate quantities of this acid greatly interferes with the free disengagement of the gases. It is also preferable to employ magnesium instead of zinc for this purpose (see page 416).

Separation of Antimony and Arsenic.

R. Bunsen dissolves the antimony and arsenic sulphides, while still moist, upon the filter in an excess of solution of potash, which must have been purified by means of alcohol. The solution, together with the concentrated washings, is introduced into a porcelain crucible, holding about 150 c.c., and a rapid current of chlorine is introduced into the liquid through a hole in the watch-glass, which serves as a cover till all the alkali is neutralised. The crucible, still covered with the watch-glass, is heated in the water-bath, and concentrated hydrochloric acid in great excess is dropped in by means of a pipette. The liquid is evaporated down to half its bulk, the loss is again made up with an equal volume of concentrated hydrochloric acid, and the liquid is again concentrated down to the half or the third, in order to expel all free chlorine. It can now be diluted to a perfectly limpid solution, by the addition of very weak hydrochloric acid, without tartaric acid, which interferes with the separation. To this solution there are now added, for every decigramme of antimonious acid probably present, about

100 c.c. of a recently prepared and *saturated* solution of sulphuretted hydrogen, when antimony pentasulphide is precipitated immediately or after a short time, according to its larger or smaller proportion. As soon as this precipitate has separated itself, the excess of sulphuretted hydrogen is immediately removed from the solution, by forcing through it a violent current of air, filtered through cotton-wool. This is easily effected by means of the blast of a glass-blowing table. To prevent loss by spiriting, the beaker must be kept covered with a perforated watch-glass, the air-pipe entering through its aperture. In about 15 to 20 minutes the gas is expelled and the liquid becomes inodorous. The precipitate is then thrown upon a weighed filter and washed with the filter-pump, the filter being filled in succession 8 or 10 times with water, twice with alcohol, 4 times with carbon disulphide, and finally 8 times with alcohol. The precipitate is dried at 110° in the salt-bath, at which temperature it remains for any length of time perfectly constant in weight. The washings even in not very experienced hands do not require more than an hour. The filtrate which contains the arsenic as arsenic acid does not retain the least trace of antimony. The antimonial precipitate may in certain cases retain quite insignificant traces of arsenic. But if, after washing with water, it is redissolved in potassium hydrate, and the process of separation repeated, the antimony is obtained free from any trace of arsenic. The estimation of arsenic in the filtrate and washings is no less simple. The collected liquid, after the addition of a few drops of chlorine, is heated on the water-bath and treated with a prolonged current of sulphuretted hydrogen both whilst hot and during cooling.

The precipitate is allowed to settle for a day at a gentle heat, and is then placed upon a weighed filter. If care has been taken to leave a sufficient excess of hydrogen sulphide in the liquid during heating and cooling, the precipitate consists of a little sulphur and arsenic pentasulphide without the least admixture of trisulphide. Before weighing it is treated exactly like the antimonial precipitate. Its composition and weight are constant after drying at 110° C.

Detection of Arsenic in Tartar Emetic.

Ignite the antimonial preparation to be tested with 4 times its weight of pure sodium nitrate, exhaust the residue with water, acidulate the solution slightly with nitric acid, concentrate by means of evaporation, and add first silver nitrate, and next, very carefully, some ammonia; the result being the formation of a more or less deep brown-red-coloured precipitate, indicating the presence of arsenic, if present. Dr. Von Ankum states that, having taken only 10 grammes of tartar emetic, containing in that quantity less than $\frac{1}{2}$ milligramme of arsenic, he was enabled to detect the latter very readily by the method described.

Detection of Arsenic in Bismuth.

Bismuth subnitrate occasionally contains arsenic. This may be detected in the following manner:—About $\frac{1}{2}$ gramme of the subnitrate is placed in a test-tube, and 1 c.c. of pure and concentrated sulphuric acid is next added, to expel the nitric acid. After this has been driven off, the tube being kept in a vertical position, from 4 to 5 c.c. of pure hydrochloric acid are added, and when the liquid has become quite clear, about 1·5 to 2 grammes of pure tin protochloride. After this salt has been dissolved, about 3 c.c. of strong and pure sulphuric acid are added; and, if the mixture does not then become very hot, it is heated just to the boiling-point. If no arsenic is present, the liquid remains clear and colourless, even after standing for some time; but if even a trace of arsenic is present, the fluid becomes at first pale yellowish, next brownish coloured, and at last metallic arsenic is deposited as a deep greyish-brown flocculent substance. Even when the arsenic is present with the bismuth in the proportion of 1 to 500,000, a colouration ensues.

Separation of Arsenic from Copper.

Mr. E. W. Parnell has carried out some accurate experiments on the best means of separating these metals.

Separation by Treatment of the Mixed Sulphides with Sodium Sulphide.—To a mixture of the two metals excess of hydrochloric acid is added; the metals are then thrown down by sulphuretted hydrogen, the mixed sulphides introduced into a flask, covered with a colourless solution of sodium sulphide, and maintained at a gentle heat on the water-bath for about 12 hours. The liquid is then filtered off, the filtrate separated, and the copper sulphide on the filter washed with boiling water, to remove every trace of soluble arsenic. The copper sulphide is then dissolved in nitric acid, the solution evaporated with a small quantity of sulphuric acid, the residue dissolved in water, again treated with sulphuretted hydrogen, the precipitate treated as before with perfectly pure sodium sulphide, and filtered. The clear solution (that will contain any arsenic that has remained with the copper in the first instance) is decomposed with hydrochloric acid, the precipitated sulphur collected, washed, and treated with ammonia, which will dissolve any arsenic sulphide that may be mixed with it. A little sodium carbonate is added to the ammoniacal solution, and the liquid evaporated to dryness in a small porcelain dish, the residue mixed with a little potassium cyanide, and the mixture examined for arsenic, by heating it in a glass tube in a slow stream of carbonic acid. A very faint mirror of metallic arsenic is obtained, probably not exceeding $\frac{1}{10}$ of a milligramme.

The filtrate from the first treatment with sodium sulphide is next decomposed with hydrochloric acid, the precipitate thoroughly washed

and dried, and carefully sublimed. No trace of copper remains as a residue. From this, therefore, it is evident that a satisfactory separation can be effected by using a colourless solution of sodium sulphide.

As ammonium sulphide dissolves small quantities of copper sulphide it cannot be used instead of sodium sulphide.

Separation by Means of Chlorine Gas in the Wet Way.—To a mixed solution of the metals arsenic and copper, excess of a solution of potash is added, and a slow stream of chlorine conducted into the liquid until the latter is thoroughly saturated with the gas. The mixture is then boiled, filtered, the insoluble part well washed, and the precipitate and filtrate examined respectively for arsenic and copper. The copper is perfectly free from arsenic; but the filtrate may contain a small quantity of copper (probably due to minute particles of copper oxide being carried through the filter, as the oxide is in an exceedingly fine condition; the quantity is very small). Care should be taken to ensure a decided excess of the chlorine, or a considerable quantity of arsenic may remain with the copper.

Separation by Means of Chlorine Gas in the Dry Way.—Excess of hydrochloric acid is added to the mixed solution, the metals thrown down by sulphuretted hydrogen, the precipitate thoroughly dried, placed in a small porcelain boat, and introduced into a glass tube; this latter passes through an air-bath, fitted with a thermometer to enable the tube to be maintained at a fixed temperature. This tube is allowed to project for about 4 inches beyond the air-bath. Perfectly dry chlorine is then conducted over the mixture, maintained at a temperature of about 200° C. for about half an hour. The projecting part of the tube, which has been almost cold during the operation, will be found to contain no trace of copper. The copper in the porcelain boat is completely soluble in weak hydrochloric acid. It is seen, therefore, from these experiments that, if proper precautions be taken to ensure perfect dryness of the mixture and the gas, a most perfect separation can be effected at a temperature of about 200° C. To avoid the formation of the globule of sulphur, or mixture of sulphur chloride and sulphur, which often takes place in the condensing tube, the precaution should be taken to first saturate the liquid with chlorine, or to use a solution of chlorine for the condensing liquid.

Separation by Igniting the Mixed Sulphides in Hydrogen. This process, conducted in the usual manner, has only for its object the estimation of the copper, unless, indeed, the amount of sulphur in the mixed sulphides is accurately known, when the amount of arsenic may be calculated from the loss. To effect the separation, the mixture is introduced into a small porcelain crucible, fitted with a perforated cover and tube for conducting the gas. A little sulphur is added, a gentle stream of hydrogen conducted into the crucible, and the mixture carefully heated by the lamp, and finally raised to bright redness. The copper subsulphide which is left will not contain the slightest trace of arsenic.

Detection of Arsenic in Copper.

The copper is dissolved in nitric acid, a small quantity of solution of ferric nitrate added, the solution nearly neutralised with sodium hydrate (not ammonia) and excess of sodium acetate added. The solution is then heated to boiling, filtered as rapidly as possible; the precipitate after being well washed is dissolved in hydrochloric acid, the solution made alkaline with ammonia and saturated with sulphuretted hydrogen and filtered from the precipitated iron sulphide. The filtrate is acidified with hydrochloric acid and let stand in a warm place for some time. The arsenic and antimony sulphides are filtered off and dried at 100°C .; the precipitates are removed completely from the paper into a small beaker, and treated with red fuming nitric acid, a few drops of hydrochloric acid being added as soon as the action has ceased. It is then diluted, filtered, the arsenic precipitated as ammonio-magnesium arsenate, and weighed as usual. If the precipitated sulphides cannot be perfectly removed from the filter-paper, the paper must be treated with nitrohydrochloric acid, filtered, and the filtrate added to the nitric acid solution.

This method is very accurate. It requires, however, some special precautions.

When the sodium acetate is added, the colour of the solution should change from pale blue to dark green; this shows that the solution has been sufficiently neutralised. The beaker must be removed from the heat immediately the solution begins to boil; if the solution be left boiling (and sometimes when it is not) a greenish-white precipitate of basic copper acetate falls. This can generally be removed by the addition of a few drops of hydrochloric acid, but in cases where it has separated on the surface of the beaker, or where it will not readily dissolve, it is best to throw out the solution and commence again.

This is very troublesome to those using this method for the first time, but after a little experience has been gained it very rarely happens.

The precipitate should have the dark red colour of ferric acetate; if it is paler it is due either to there not being sufficient iron, or to the co-precipitation of some basic copper acetate. The filtrate should be blue or pale green; sometimes it is dark green and turbid, from the presence of iron acetate carried through the filter; in that case the first portions must be passed through the filter again.

The precipitate must be washed till it is free from copper, and when it is dissolved in hydrochloric acid the solution must have the yellow colour of ferric chloride. If it is all green, the solution must be neutralised, a little more sodium acetate added, and the iron and arsenic reprecipitated.

With equal quantities of iron and arsenic a small quantity of

arsenic remains in solution, and the iron arsenic precipitate is of a pale colour. With 1.5 part of iron to 1 of arsenic the precipitation is complete. In order to make sure it is well to add about twice as much iron as it is expected there is arsenic present. Then, even if a little iron remains unprecipitated, all the arsenic will be thrown down.

Since copper sulphide retains so much arsenic, it might be expected that iron sulphide would act in a similar manner, but it does not; if there be no copper present, the precipitate is quite free from arsenic, but if copper is present a considerable quantity of arsenic may be retained. Hence the importance of thoroughly washing the acetate precipitate and reprecipitating it if necessary.

Detection of Arsenic in Commercial Copper.

As even in the most satisfactory performance of Reinsch's test for arsenic—the deservedly favoured test of English toxicologists—there is always some, although but an extremely small quantity of the copper wire, foil, or gauze dissolved, and as commercial copper is rarely quite free from arsenic, and sometimes contains a very notable proportion thereof, it is important that the copper to be used in medico-legal researches as a precipitant for arsenic should be specially tested as to its purity. But as, in the ordinary mode of experimenting by Reinsch's process, the amount of metal dissolved is scarcely appreciable, it is quite unnecessary to submit any considerable quantity of it to examination. If a solution of 4 or 5 grains of the copper does not yield any evidence of arsenic, it is quite pure enough for the purpose, even though a little arsenic should be recognised in the solution of a larger quantity.

As a means of detecting traces of arsenic in copper, Dr. Odling considers the following process to be superior to any hitherto proposed in conjoint delicacy and rapidity of operation :—

A few grains of the copper cut into fine pieces are placed in a small tube-retort, with an excess of hydrochloric acid, and so much ferric hydrate or chloride as contains a quantity of iron about double the weight of the copper to be acted upon. The mixture is then distilled to dryness, some care being taken at the last to prevent spirting.

The whole of the copper is in this way quickly dissolved, and any arsenic originally contained in it carried over in the form of arsenic chloride, which may be condensed in a little water with the excess of aqueous hydrochloric acid. The resulting distillate is then tested for the presence of arsenic, by treating it with sulphuretted hydrogen, or preferably by boiling in it a fresh piece of clean copper foil or gauze. In some cases the residue left in the retort may be treated with a little fresh hydrochloric acid, again distilled to dryness, and the distillate collected and tested along with that first produced.

Most oxidisers other than ferric chloride are objectionable, as by

their reaction with hydrochloric acid they give rise to free chlorine, which passes over with the distillate, and renders it unfit for being immediately tested either with sulphuretted hydrogen or fresh copper. Cupric oxide or chloride, on the other hand, is scarcely active enough for the purpose, while the dissolution of copper in hydrochloric acid brought about by mere exposure to the air is extremely tedious.

It may be as well to add that ferric chloride is rendered quite free from arsenic by evaporating it once or twice to dryness with excess of hydrochloric acid.

Estimation of Small Quantities of Arsenic in Sulphur.

H. Schaeppi proceeds as follows:—Ten grammes of sulphur, pulverised as finely as possible, are covered with hot water, and a few drops of nitric acid digested for some time, filtered and washed till the washings have no longer an acid reaction. Thus calcium chloride and sulphate are removed, and calcium sulphide, if present, is destroyed. The sulphur thus prepared is covered with water at 70° to 80°, a few drops of ammonia are added, and the mixture is digested for a quarter of an hour. All the arsenic present as sulphide is dissolved, and the ammoniacal liquid is variously treated according to the degree of accuracy required. For perfectly accurate estimations the ammoniacal solution is mixed with silver nitrate, and all the sulphur present in the state of arsenic sulphide is thrown down as silver sulphide, acidified with nitric acid, filtered, and washed. The precipitate of silver sulphide is dissolved in hot nitric acid and estimated as silver chloride. From the weight of the latter the arsenic sulphide is calculated. As a less accurate but more rapid method, the ammoniacal solution of arsenic sulphide is cautiously neutralised with pure dilute nitric acid and considerably diluted. It is then titrated with decinormal silver nitrate till a drop of the solution is turned brown with neutral chromate. The arsenic is easily calculated from the quantity of silver nitrate consumed. For very rough estimations it is sufficient to treat 10 grammes of finely-ground sulphur with nitric acid, to extract with ammonia, and to add silver nitrate. From the intensity of the colour, or the quantity of the precipitate of silver sulphide, it may be judged if the sulphur is approximately free from arsenic, or strongly contaminated. The author states that, contrary to the general belief, reddish-yellow sulphur is more free from arsenic than such as is of a full yellow colour.

TELLURIUM AND SELENIUM.

Separation of Tellurium from Selenium and Sulphur.

No difficulty occurs in separating tellurium from sulphur. In fact, although they are frequently found together in nature combined with bismuth, they are not isomorphous, and, although there is a simple

relation between their combining numbers, there are but few analogies between their compounds, none of which are found to crystallise in the same system. The analogies between sulphur and tellurium would, perhaps, not have been considered obvious did not selenium form a connecting link between the two, offering, in many respects, great similarities with the former, and, in other respects, with the latter element. Both selenium and tellurium are precipitated from tellurous and selenious acids, by means of sulphurous acid, tin protochloride, metallic tin, and several other metals. The difficulties arising in the separation of tellurium, selenium, and sulphur consist, therefore, in the analogies between tellurium and selenium, and between sulphuric and selenic acids.

The usual way of separating selenium from tellurium is based upon the insolubility of barium seleniate. But the difficulties in preparing selenic and telluric acids, and the slight solubility of the barium tellurate, make this process a very tedious one. A mixture of barium seleniate and sulphate is sometimes separated by reducing the former in a current of hydrogen and dissolving the selenide in hydrochloric acid.

Some years ago, Dr. Oppenheim proposed an easier method of separating these elements, based upon the different way in which they are acted upon by potassium cyanide. Sulphur is dissolved when fused with this compound and not precipitated by hydrochloric acid. Selenium—as the writer was the first to observe—is likewise dissolved, but is reprecipitated by any acid. Tellurium not only refuses to form a tellurocyanide when fused with potassium cyanide, but takes the place of the cyanogen therein, forming potassium telluride, which dissolves in water, with a purple colour, and is speedily decomposed, by the action of the air, into potash and metallic tellurium. This process, however, is imperfect, on account of a slight loss, which was first ascribed to the volatility of the elements at the temperature employed. The loss, however, occurs chiefly on the side of tellurium, which, of the three elements, is the least volatile, and it is owing principally to part of the tellurium being oxidised and dissolved as potassium tellurate.

Instead of melting the elements with potassium cyanide, it suffices to heat them with a solution of the salt. Sulphur and selenium are thus completely dissolved. A small proportion of tellurium forms potassium tellurite, and the rest remains in the metallic state. The separation of the elements is, therefore, conducted in the following manner:—A mixture of them, reduced to a fine powder, is boiled with a solution of potassium cyanide in a water-bath for about 8 hours. Tellurium is then collected on a filter. Selenium is precipitated in the filtrate by means of hydrochloric acid, and the second filtrate is mixed with sodium sulphite, heated, and allowed to stand for 24 hours. The portion of tellurium which has been dissolved as potassium tellu-

rite is thus completely precipitated. It is then added to the other portion collected on the filter, dried in the water-bath, and weighed. Selenium is estimated in a similar manner, whilst the quantity of sulphur present is indicated by difference.

The same method may be employed for separating selenium from metals not soluble in potassium cyanide. But if iron, copper, or other metals are present, which form soluble compounds with the reagent, partly precipitated by hydrochloric acid, it is necessary to dissolve the mixture of the elements in acids and to add a quantity of ammonium sulphide sufficient to dissolve the selenium and tellurium. They must then be precipitated from this solution as sulphides and treated with potassium cyanide, as described above. When selenium sulphide is acted upon by potassium cyanide, the selenium is first dissolved, and a residue of sulphur remains behind, which disappears but slowly. The red modification of selenium is dissolved more easily than the black. Selenious acid cannot be reduced by being boiled with potassium cyanide.

M. V. Schroetter, in analysing telluriferous minerals, treats the ore with aqua regia and precipitates the gold with oxalic acid or glycerine. The liquid after removal of the gold is treated with sulphurous acid, which precipitates selenium and tellurium, the former element being all contained in the first portions of the precipitate. The mixed precipitate is treated with nitric acid; the tellurous acid is filtered off, and the filtrate which contains the selenium is distilled. In the precipitation of tellurium by sulphurous acid, a point comes when the precipitation ceases, though tellurium is still held in solution. This portion falls on diluting with water.

Preparation and Quantitative Estimation of Tellurium.

Crude tellurium is oxidised in heat with nitric acid, mixed with water, boiled up, and set aside for 24 hours. During this time most of the tellurium separates out as tellurous acid. This, together with the sand, is filtered off, dissolved in hydrochloric acid, precipitated with sulphurous acid, the separated tellurium extracted with concentrated hydrochloric acid, filtered, and dried. The filtrate is further treated with sulphurous acid, and the impure tellurium separated out is treated further like crude tellurium. The tellurium thus obtained is pure enough for most purposes, but if a chemically pure tellurium is required it must be distilled in a current of hydrogen.

Mr. L. Kastner gives the following method for the estimation of tellurium:—The tellurium precipitated by sugar is collected on a small filter and washed. It is then transformed into tellurous acid by moistening with a mixture of 2 volumes nitric acid, 1 volume water, and 8 drops of sulphuric acid per 10 c.c. of mixture. The tellurous acid in acid solution is evaporated to dryness in a porcelain capsule and weighed.

For the detection of tellurium in ores which contain it as gold telluride, G. Kustel uses sodium amalgam. The powdered ore is placed in a capsule with a little water and mercury, and afterwards with a little sodium amalgam. If tellurium is present, the water takes a violet colour. If it contains sulphur, the water blackens silver-foil. If iron sulphide is present, the violet colour produced by sodium telluride may be masked by the precipitate occasioned. In such cases the water is poured off, a fresh quantity of water added, and the test is recommenced with a fragment of sodium amalgam.

Separation of Tellurium from Gallium.

The liquid containing tellurium in the state of tellurous acid is mixed in the cold with a sufficiency of hydrochloric acid and saturated in the cold with sulphuretted hydrogen. Tellurium sulphide is precipitated, whilst the gallium is found in the filtrate, which is not, however, always absolutely free from tellurium. In an accurate analysis the clear liquid should therefore be boiled for some minutes, whilst a current of hydrogen sulphide is passed through it, and the slight traces of tellurium sulphide obtained by this second operation are collected on a filter. When the volume of the filtrate is considerable, it is preferable to begin by concentrating to a small bulk before treating, hot, with sulphuretted hydrogen.

Estimation of Selenium.

Sulphurous acid is the best reagent to precipitate selenium when this element exists in the state of selenious acid; the precipitation should be performed in the presence of hydrochloric acid. Sulphurous acid may also be replaced by phosphorous acid, likewise in the presence of hydrochloric acid; but the reduction takes place much slower than when sulphurous acid is used.

As pointed out above, selenium may be estimated by fusing the body containing it with potassium cyanide, dissolving the fused mass in water, and then supersaturating the solution with hydrochloric acid, which effects the complete precipitation of the selenium at the end of a few hours. The fusion ought to be performed in an atmosphere of hydrogen; it is advisable, when the substance contains free selenious acid, to previously saturate this acid with an alkaline carbonate, so as to avoid volatilising small portions before the potassium cyanide has had time to react upon it.

The solution obtained by treating the fused mass with water contains potassium selenocyanide, together with a small quantity of selenide; it is necessary, on this account, to boil the liquid for some time before the addition of hydrochloric acid, to convert the selenide into selenocyanide. Without this precaution, a portion of the selenium might be disengaged in the form of seleniuretted hydrogen.

When the selenium acids are fused with alkaline carbonates in an

atmosphere of hydrogen they are reduced to alkaline selenides ; from a solution of these latter a slow current of atmospheric air entirely precipitates the selenium. This process may serve for estimating selenium, but it is less accurate than the preceding.

Sulphuretted hydrogen completely precipitates selenious acid from its solutions in the form of selenium disulphide, from the weight of which the selenium may be estimated.

Selenious acid may be estimated in its aqueous solution, or, in the presence of nitric and hydrochloric acid, by simple evaporation, taking care not to exceed a temperature of 100° C., above which a portion of the acid may volatilise.

The ordinary process for the estimation of selenic acid, which consists, as is known, in precipitating this acid as a barium salt, is, according to Rose, far from deserving the confidence with which it is usually regarded. On the one hand, selenate of barium is much more soluble than the sulphate ; on the other hand, it possesses, in a much greater degree than this latter salt, the property of carrying down with it considerable quantities of the soluble salts which are contained in the liquid. It is better to reduce the selenic acid to selenious acid with hydrochloric acid, and then to precipitate the selenium with sulphurous acid.

When it is desired to estimate the selenic acid in an insoluble combination, particularly in barium selenate, this combination is decomposed by an alkaline carbonate ; the transformation into an alkaline seleniate takes place even in the cold, and it is then easy to reduce the selenic to selenious acid by means of hydrochloric acid.

Separation of Selenium from Metals.

Selenium cannot be separated from the metals with which it is combined when the sulphides of these metals are insoluble in ammonium sulphide, by making use of the solubility of selenium in this reagent. The insoluble metallic sulphide is almost always mixed with selenide. Most frequently, selenium may be separated from metals by heating the mixture in a current of chlorine ; the selenium chlorides are sufficiently volatile to render the separation generally easy. In acid solutions of the selenites of metals not precipitable by sulphuretted hydrogen, the selenium may be precipitated by this gas in the state of selenium sulphide.

To estimate the alkalis and alkaline earths combined with selenium acids, it is sufficient to fuse them with ammonium chloride. The alkali or alkaline earth remains in the state of chloride. One single fusion, or two at the most, are sufficient to drive off all the selenium.

Separation of Selenium from Gallium.

According to circumstances, one of the two following processes may be employed. The selenium should be present in the state of selenious acid.

a. The solution, rendered distinctly acid with hydrochloric acid, is treated with a current of hydrogen sulphide, whilst the temperature of the solution is gradually raised to a boil. The selenium sulphide is collected on a filter, and the filtrate yields gallium chloride on evaporation.

b. The liquid is acidified by hydrochloric acid, and the selenium is reduced by means of a current of sulphurous acid passed through the hot solution. The liquid is kept at a boil for 10 to 15 minutes, which agglomerates the selenium and prevents it from passing through the pores of the filter. The gallium is found in the filtrate.

Preparation of Selenium from Seleniferous Flue Dust.

This is a mixture of selenium and metallic selenides with soot, sand, &c., which accumulates in some of the flues leading to the leaden chambers from the burners where some kinds of pyrites are burned. With some ores at Mansfeld it contains as much as 80 or 40 per cent. of selenium.

The dark-coloured mass, after being first moistened with sulphuric acid and then washed and thoroughly dried, is placed in a porcelain or luted glass retort. It is then strongly heated, the temperature towards the end of the operation approaching that at which the glass softens. Most of the selenium will now distil over perfectly pure.

The residue, consisting of selenides mixed with carbon and other impurities, should be dissolved in hydrochloric acid containing a little nitric acid. Precipitate the iron and copper with caustic soda, filter, and precipitate the selenium in the filtrate either by saturating the liquid with sulphurous acid, or by evaporating with an excess of sal-ammoniac and heating until this begins to volatilise. The alkaline salt is then removed with water. If the selenium were precipitated by sulphurous acid before removing the copper from the liquid the precipitate would retain somewhat considerable quantities of this metal.

Detection of Sulphur in Selenium.

Dissolve the selenium in very strong nitric acid, add a little hydrochloric acid and boil. Any sulphur which may be present can then be detected by barium chloride, as it will be in the form of sulphuric acid. Remove the excess of barium from the filtered liquid by addition of sulphuric acid, and reduce the selenium with sulphurous acid.

Preparation of Selenious Acid.

Act upon selenium with concentrated nitric acid, and evaporate the solution until selenious acid begins to sublime; the residue is dissolved in water. This solution may contain, besides selenious acid, some sulphuric and selenic acids; in order to separate these from each other, baryta-water is added. Since barium selenite is readily soluble in an excess of selenious acid the addition of baryta-water is continued until a small quantity of the fluid, having been filtered, no longer gives a permanent precipitate on the addition of more baryta-water. The fluid, having been filtered, is evaporated to dryness and sublimed; the selenious acid thus obtained is quite free from selenic and sulphuric acids.

Preparation of Selenic Acid.

Selenic acid is prepared from selenious acid by dissolving the latter in water, and precipitating the solution with silver nitrate; the insoluble silver selenite is shaken up with a mixture of water and bromine until the latter is in slight excess. The solution, having been filtered and concentrated by evaporation, yields selenic acid, free from sulphuric or selenious acid.

Another good method of preparing selenic acid is given by Wöhler:—Saturate selenious acid with copper carbonate, and then pass a current of chlorine into the liquid, until the precipitate is completely dissolved. The solution, after being again saturated with copper carbonate, is concentrated by evaporation; the copper seleniate is then precipitated by alcohol, in which the copper chloride dissolves. Wash the copper seleniate with alcohol, then dissolve in water and remove the copper by a current of sulphuretted hydrogen.

CHAPTER X.

GOLD, PLATINUM, PALLADIUM, IRIDIUM, OSMIUM, RHODIUM,
RUTHENIUM.

GOLD.

Detection of Minute Traces of Gold in Minerals.

THE large number of non-auriferous or but slightly auriferous specimens of quartz and pyrites which have sometimes to be examined for gold renders it desirable that some quicker, less laborious, and, if possible, more exhaustive, method of analysis than the current one (that by amalgamation) should be employed. After many experiments, Mr. Skey, Analyst to the Geological Survey of New Zealand, has devised a plan which gives very good results, even when small quantities of mineral are operated on. He employs iodine or bromine for the purpose of dissolving out the gold. Both of these substances differ from chlorine especially in their relatively feeble affinities for hydrogen, so that there is less fear that from the generation of hydrogen acids any great preponderance of other matters would be dissolved along with the gold. Either of these substances can be safely and advantageously employed for the separation of gold from its matrix.

The following particulars of experiments made in this method will be useful in showing what is approximately the smallest quantity of gold that can be positively separated and identified, when operating upon a limited quantity.

1st. Two grammes of roasted 'buddle headings' from a quartz mine at the Thames, N.Z., known to contain gold at the rate of 1 ounce or so to the ton, was well shaken for a little while with its volume of alcoholic solution of iodine, then allowed to subside. A piece of Swedish filter-paper was then saturated with the clear supernatant liquid, and afterwards burned to an ash; the ash, in the place of being white, as it would be if pure, was coloured purple; the colouring matter was quickly removed by bromine—a clear indication of the presence of gold. The time occupied by the whole process was 20 minutes.

2nd. One gramme of the same 'buddle headings,' mixed with such a quantity of earth as to reduce the proportion of gold present to 2 dwts. per ton, was kept in contact with its own volume of the tincture of

iodine for 2 hours, with occasional stirring; a piece of filter-paper was then saturated with the liquid, and dried, five times consecutively, and finally burnt off as before: in this case, also, the colour of the residual ash was purple, and it gave the reaction of gold.

8rd. Thirty-two grammes of siliceous hæmatite, finely pounded, were thoroughly mixed with precipitated gold to the amount of 2 dwts. per ton, then ignited and treated with bromine-water. After 2 hours the solution was filtered, and evaporated to a bulk of 20 minims; this gave a good reaction of gold to the 'tin chloride' test.

4th. One hundred grammes of the hæmatite, with precipitated gold at the rate of $\frac{1}{2}$ -dwt. per ton, treated as before, but this time well washed at the expiration of 2 hours; the washings evaporated along with the first filtrate gave a fainter, but still decided, reaction of gold to the same test.

5th. Iodine, as tincture, substituted for bromine in Experiments 8 and 4, gave similar results; the only variation made was, that, as a precautionary measure allowing for its slower action, they were kept in contact for 12 hours.

Careful experiments have been made to compare the results of the common amalgamation process with the foregoing, and it has been found that it is not certain, with the same expenditure of labour, to get reliable indications of gold, when present in less quantity than 2 dwts. per ton, operating upon about 100 grammes of material.

In summing up the results of these experiments, it appears, then, that for qualitative examinations for gold, or for quantitative estimations in certain cases, iodine and bromine are each superior to mercury. It also appears that a proportion of gold equal to $\frac{1}{2}$ dwt. per ton, upon a bulk of 100 grammes (about 4 ounces) of ferruginous matters, can be easily and rapidly detected. Of course, by operating upon larger quantities, gold could be discovered by this process, were it present in far less quantities, but this is sufficiently near for the majority of cases.

These processes are especially adapted for the separation of gold from sulphides, as the preliminary roasting is extremely favourable to them, the loss in the substitution of oxygen for sulphur amounting to 25 per cent. by weight, while the volume remains constant (or nearly so); hence there is a corresponding porosity in the product, by which every particle of it is thrown open to contact with the solution. This mechanical accessibility obviously cannot be taken advantage of by mercury.

With sulphides these processes are practically exhaustive, while, at the same time, the simultaneous extraction of other matters is so trifling, that the proper tests for gold can be safely applied directly to the concentrated solution. In the roasting of pyrites it is necessary to raise the temperature towards the end to a full red heat, in order to decompose the ferruginous sulphates, since if these remained iron

would get into the solution. In the case of an excess of calcium carbonate being present, it is proper to gently re-ignite the roasted mineral, &c. with ammonium carbonate, or much lime might get into the iodine or bromine solution. On the other hand, a very high temperature is to be avoided, for a considerable quantity of fine gold can escape detection in this way, by the partial vitrification of the more fusible of the silicates.

The identification of gold by the combustion of its salts with filter-paper seems to promise a rapid method of estimating it, comparatively, by the aid of a series of prepared test-papers, representing gold in different degrees of dilution.

M. Sergius Kern proposes the following method of detecting gold. The gold of the sample under analysis is first separated from foreign metals, and next converted by means of sodium chloride into sodio-gold chloride; the solution is then concentrated by evaporation. In order to detect gold, an aqueous solution of potassium sulphocyanide is used, containing for 1 part of the salt about 15 to 20 parts of water. About 6 grammes of this solution are poured into a test-tube, and some drops of the concentrated solution obtained by treating the samples as described above are added. If gold is present a red-orange turbidity is immediately obtained, which soon falls in the form of a precipitate; on gently heating the contents of the test-tube the precipitate dissolves, and the solution turns colourless.

The reagent is so delicate that one drop of a solution of sodio-gold chloride (1 gramme of the salt dissolved in 40 grammes of water) gives a very clear solution.

Colonel Ross was the first to give gold among the metals whose sublimates can be obtained with the common blowpipe, which is owing to the fact that it can be easily produced and seen on aluminium, though not on ordinary charcoal. Ross appears to have produced it only from a ball of gold and lead, and he makes no mention of getting it from pure gold. In his book is a coloured representation of a very beautiful sublimate obtained from gold with a little lead, and it appears that he regards the lead as necessary for the operation, attributing the colours to gold *oxide*, formed and volatilised by the action on the gold of the lead oxide produced. Mr. Blossom finds that a very fine gold sublimate can be obtained in 2 or 3 minutes by strongly heating a little ball of perfectly pure gold on a charcoal-slip on the ledge. The mouth-blowpipe suffices, but it is got more quickly, and better, by using a stand blowpipe and hand-blower. After 2 minutes' blowing the appearance on the plate is as follows:—Nearest the charcoal, where the heat on the plate had been greatest, is a small arch of pale yellow colour, just a thin film of gilding over the aluminium. Beyond this is a strip, $\frac{1}{4}$ to $\frac{1}{2}$ inch wide, of a beautiful violet or purplish-violet colour, and dotted all over the sublimate are little specks and splashes of gold carried over mechanically. By heating for a much longer

time, with frequent stopping to let the plate cool, very fine sublimes may be produced. The purplish violet obtained is clearly the same as the deposit on white paper held under a fine gold wire through which a powerful electric discharge passes; and it is certainly interesting to be able to obtain the same appearance by means of the blowpipe.

Estimation of Gold in Pyrites.

Melt 100 grammes pyrites with 16·6 grammes fine iron turnings under a layer of common salt. The monosulphide formed is powdered, and attacked with dilute sulphuric acid in a gas apparatus, the sulphuretted hydrogen being received in ammonia. The matter insoluble in acid is collected, washed, dried, and roasted. It is then mixed with borax and about 2 grammes granulated lead, and the mixture melted in a muffle until the lead collects in a single globule floating in ferruginous scoræ. This globule is detached and submitted to cupellation.

On this process it may be remarked that by simply fusing the pyrites alone at a strong heat, with such flux as the gangue, if any is present, may require, a very much smaller regulus will result, equally sure to contain all the gold and equally suitable for treatment with acid.

The simplest mode of treating the insoluble residue after acting upon the regulus with acid, is to collect it on a small filter, dry it, lay it upon a scorifier, cover with assay-lead, fuse, and scorify in a muffle, finally cupelling the lead-button. This method of assay may be advisable in cases where *very small* amounts of gold are to be estimated; but in most cases it cannot compare, for convenience, with the direct treatment of the ore by scorification or by reduction of litharge, concentration of two or three lead-buttons so obtained, and cupellation.

The following method may be useful in certain cases:—One pound, or even 18 ounces (avoirdupois) of fine marble-dust is mixed with 8 ounces of finely pulverised and sifted pyrites; the whole is then re-sifted and put into a Hessian crucible, which should be about one-third filled by the mixture. The crucible is set as usual on a fire-brick, and a fire of hard coal is made around it, the coals being heaped up to within an inch of the top. The crucible is covered with a piece of brick, or a piece of sheet-iron. During the first half-hour the contents should be stirred once or twice. As the fire grows brisker the carbonic acid evolved keeps the contents of the crucible in brisk ebullition, and the mixture should be stirred well every 5 or 10 minutes. On stirring during this time, the iron rod used seems to meet with but little resistance from the light mass, but at the end of about 1½ hour the evolution of gas suddenly ceases, the red-hot mass becomes heavy, sinks, and requires considerable force to keep it stirred. It must be stirred well and vigorously, however, for about half an hour, not leaving it unstirred for more than a minute, otherwise the mass will fuse or cake, and the assay will be almost inevitably ruined.

When a sample taken out in an iron spoon gives off *no* smell of

sulphur, the entire contents of the crucible must be turned into a stoneware pot, or a wooden bucket, half filled with water, and well stirred. When the powder—which should be uniform and free from lumps or fused pieces—has settled, the water must be poured off, the wet mass allowed to drain, and then transferred to a large earthen bowl or porcelain mortar. Here it is to be amalgamated with about 2 ounces of mercury, to which a little bit of sodium amalgam has been added. The amalgamation, as well as the stirring in the fire, is a tedious process. It does not consist in merely grinding with a pestle the mercury in among the particles of the roasted ore, but this ore itself must be ground in contact with the mercury until the particles are so fine that they will float suspended in water for several seconds. At the end of, say, 10 minutes' thorough grinding, the contents of the bowl are to be brought into one mass in the bottom of the vessel, the bowl then sunk in a tub of water, and the contents 'washed down,' an operation not easily described, but familiar enough to every old Californian. It consists essentially in shaking the bowl half-full of ore and water in such a way that the mercury, gold particles, and unground ore sink to the bottom, while the light and finely-ground ore is floated off into the tub. The ore remaining is re-ground and re-washed, and these processes are repeated till nothing but the mercury remains in the bottom of the bowl or mortar. This mercury is then dried with filter-paper and heated in a porcelain capsule over a Bunsen flame, very gently, until it is sublimed and the gold remains behind. The film of gold may then be scraped up and melted, with a little sodium borate and potassium nitrate, in the very smallest-sized Hessian crucible, either with the foot blowpipe or in a charcoal furnace, by which means a round, clean button of gold suitable for weighing will be obtained.

This method is tedious, laborious, and, to a considerable degree, uncertain, but it will indicate the presence of gold, and will bring it out in a weighable form from pyritic ores, where the assay by smelting will not show a trace of the precious metal; and when the fire assay shows a certain percentage this will invariably bring out a larger amount.

Separation of Gold by Quartation with Zinc.

On melting the zinc with the alloy, in an open porcelain crucible, the former is partially oxidised, the film of oxide hindering the contact of the metals. If the fusion is performed under a layer of resin, the vapours become ignited, and the resin is often burnt away before the fusion is effected. Even in a covered crucible the resin is also soon volatilised, whilst particles of carbon are deposited on the lid and the sides, and falling back into the crucible contaminate the alloy. The finer particles of carbon render the solution in nitric acid turbid, and cannot be entirely removed by washing. Balling, therefore, modifies

Jüptner's process as follows:—He uses cadmium, which is more readily fusible, for quartation, instead of zinc, and takes potassium cyanide as a cover. The metals unite readily under the melted cyanide at the heat of a Berzelius spirit-lamp, and a homogeneous regulus is soon obtained. The crucible, when cold, is placed in a beaker, and the potassium cyanide is dissolved in water. The solution is poured away and the metal is washed with water. It is then introduced into a flask and boiled once with nitric acid of sp. gr. 1·2, and then thrice with nitric acid of sp. gr. 1·8. The cadmium is completely dissolved. Two and a half parts of this metal suffice for quartation. The granule of gold retains the form of the original metal, and is transferred to a small crucible for ignition.

Estimation of Gold and Silver in Alloys, after Quartation with Cadmium.

Weigh off two portions of the alloy, each of 25 grammes, and place them with the cadmium in small porcelain vessels. A piece of potassium cyanide is melted in a porcelain capsule over the flame, and the metal thrown in. The melting together takes place readily, and is complete in a few minutes. By changing with two or three porcelain capsules, and having a vessel with warm water at hand, in which the melt is dissolved when sufficiently cool, twenty to thirty meltings can be executed in an hour. The two metallic granules are now thrown together into a small long-necked flask, in which is nitric acid of sp. gr. 1·8; a piece of wood charcoal is introduced to prevent bumping—which would rupture the globules—and heat is gently applied. The first solution lasts rather long, according to the proportion of gold; e.g. an hour in case of fine gold. The solution is poured off, the boiling repeated with nitric acid of sp. gr. 1·8 for 10 minutes, the liquid again poured off, the globules rinsed with water, which is poured off, and the flask filled with water is inverted into a porous earthen crucible, dried and ignited strongly, proceeding as in cupellation. In most cases the globules can be weighed separately. Silver is estimated in the solution by titration with ammonium sulphocyanide.

PLATINUM.

Detection of Small Quantities of Platinum.

When potassium iodide is added in slight excess to a solution of platinum chloride, the platinum iodide is dissolved, and, should the solution be concentrated, a dark red liquid is produced. F. Field shows that very minute traces of platinum can be detected in this way, and in many cases where that metal is in combination with a very large excess of other metals it may be distinctly recognised. To show the delicacy of the test, 0·1 gramme of platinum was converted into chloride, evaporated carefully to dryness, care being taken that

every trace of nitric acid was expelled. This was dissolved in 1000 c.c. of water, each c.c. therefore containing $\frac{1}{100000}$ part of platinum, to which a drop of potassic iodide imparted immediately a dark rich rose colour, strikingly resembling a concentrated solution of cobalt nitrate. 10 c.c. of this was made up to a litre (1000 c.c.), so that every c.c. contained 0.000001, or $\frac{1}{1000000}$ of platinum. One part of platinum in 2,000,000 of liquid can be detected by this test. A drop or two of acid added to the solution accelerates the development of the colour. Sulphuretted hydrogen, sodium sulphite and thiosulphate, sulphurous acid, mercuric chloride, and certain other reagents immediately destroy the colour. When the pink solution is heated the tint disappears.

Purification of Platinum.

The tendency of platinum to alloy with other metals at a temperature far below its fusing-point is sufficiently well known to every user of platinum crucibles. It is equally well known that iron, &c., which has been absorbed by platinum cannot be removed, except superficially, by the action of hydrochloric acid for instance, nor even by heating in acid potassium sulphate. Stas, in his memoir on the atomic weight of silver, &c., states that he purified his platinum vessels from iron by causing them to come in contact, at a red heat, with the vapour of ammonium chloride. The process had to be repeated as often as any yellow sublimate was formed. Instead of ammonium chloride, Mr. Sonstadt puts dry double ammonium and magnesium chloride in the platinum vessel intended for purification. The vessel is then heated to about the fusing-point of cast-iron for about an hour. In this process not only is ammonium chloride vapour given off for a long while with the double salt, at a temperature much above that at which ammonium chloride alone volatilises, but when that salt is completely expelled the magnesium chloride remaining is perpetually being decomposed with evolution of free chlorine, and, frequently, the formation of a crystalline crust of periclase lining the crucible.

Platinum thus purified is softer and whiter than ordinary commercial platinum. The method is not only available for the removal of iron, but retrieves crucibles that have become dark coloured and brittle from exposure to gas flame, as well as crucibles that have been attacked by silicates during fusion of these with sodium carbonate. In his original paper on this subject Mr. Sonstadt draws attention to the extreme facility with which platinum becomes impure by heating in contact with matters containing only a very small proportion of some substance capable of attacking the metal. Thus a platinum crucible becomes sensibly impure after prolonged ignition at a high temperature, bedded in commercial magnesia. On the other hand, a platinum crucible has been kept at a constant weight to the tenth of a milligramme over a series of intense ignitions, when the precaution had been taken to bed it in chemically pure magnesia.

Analysis of Platinum Ores.

Platinum ores contain the following substances :—

1. Sand. The whole of the sand is never removed by washing the ore; the sand contains quartz, zirconium, iron chromate, and, in the Russian ores, iron titanate.

2. Iridium osmide.

3. Platinum, iridium, rhodium, ruthenium, and palladium, combined no doubt in the form of an alloy.

4. Copper and iron which exist in the ores in a metallic state, for the iron found in the sand is not soluble in acid.

5. Gold and, oftener than is supposed, a little silver. The latter metal is generally found with the palladium, and it is very rarely that palladium is obtained quite free from silver when it is prepared by the old processes.

MM. Deville and Debray's Method of analysing these ores is as follows :—

1. *Sand*.—To estimate the sand take a small assay crucible, or an ordinary crucible with smooth sides, and melt in it a little borax, so as to glaze the inside. Now introduce from 7 to 10 grammes of pure granulated silver and 2 grammes of the ore, fairly taken and weighed very accurately. Over the platinum put 10 grammes of fused borax, and one or two small pieces of wood charcoal. The silver is now melted, and care must be taken to keep it for some time a little hotter than the melting-point, so that the borax may be very liquid, and may dissolve the vitreous matters which accompany the platinum and constitute the sand. The crucible is now allowed to cool, and, when it is cold, the button, which will contain the silver, osmium, platinum, and all the other metals, is detached, and if necessary digested for a time with weak hydrofluoric acid to remove the last portions of borax. It is now heated to a faint redness and then weighed. The weight of the button subtracted from the sum of the weights of the ore and silver employed will give the amount of sand contained in the ore. It is very important to know this amount, for it represents the only matter absolutely destitute of value which the ore contains; and this simple operation may be considered the most important performed in estimating the value of an ore. It is, besides, performed so quickly that it is as well to do at the same time two or three specimens, taken from different parts of a lot of platinum powder.

2. *Iridium Osmide*.—Another 2 grammes of the ore weighed very accurately are treated with aqua regia at 70° C. until the platinum is entirely dissolved. The aqua regia must be renewed occasionally for 12 or 15 hours, or until it is no longer coloured. It is best to perform this operation in a large beaker, and to place a cover over it to prevent loss. The solutions must be decanted with the greatest care from the metallic spangles of the iridium osmide and the sand which remain

at the bottom of the beaker. If necessary it may be filtered, but as little as possible of the osmide must be allowed to go on the paper. The insoluble residue must be washed by decantation, then dried and weighed, after having added what remained on the filter. By subtracting the weight of this residue from the weight of the sand obtained in the former operation, the weight of the iridium osmide is obtained.

The button obtained in estimating the sand might be employed in this operation. In that case it is necessary to dissolve out the silver with nitric acid, and then proceed with the residue, as just directed.

8. *Platinum and Iridium*.—The solution in aqua regia obtained in the last operation is evaporated to dryness at a low temperature, and the residue is redissolved in a small quantity of water (if it should not entirely dissolve in the water some more aqua regia must be added, and the evaporation repeated), to which is added about twice its bulk of pure alcohol; lastly add a great excess of sal-ammoniac in crystals. The whole is now slightly warmed, to complete the solution of the sal-ammoniac; it is then stirred, and afterwards set aside for 24 hours. The orange-yellow, or even reddish-brown precipitate which is formed, contains most of the platinum and the iridium, but some remains in the solution. The precipitate must be thrown on a filter and washed with alcohol. Afterwards the filter is dried in a platinum crucible, placed, for greater safety, within a larger one, and afterwards heated by degrees to low redness. The crucibles are now uncovered, and the filter is burnt at the lowest possible temperature. Once or twice after the incineration of the filter a piece of paper saturated with turpentine should be introduced into the crucible, by which means the iridium oxide will be reduced and the expulsion of the last traces of osmium will be effected. The crucible is now heated to whiteness until it no longer loses weight, or the reduction is finished in a current of hydrogen.

The liquid separated from the platinum-yellow by filtration is evaporated until the ammonium chloride crystallises in large quantity. It is allowed to cool, then decanted, and on a filter is collected a small quantity of a deep violet-coloured salt, which is the iridium ammonio-chloride, mixed with a little of the platinum salt. This is first washed with a solution of sal-ammoniac and then with alcohol. The salt is then ignited, and, if necessary, reduced by hydrogen like the platinum salt. The mixture of platinum and iridium, obtained by the two reductions, is then weighed. The two metals are now digested at about 40° or 50° C., in aqua regia, diluted with about 4 or 5 times its weight of water—the aqua regia being renewed until it is no longer coloured. The residue is pure iridium. To obtain the weight of the platinum, the weight of the iridium is subtracted from that of the mixture of the two. This method of separating the two metals is

very accurate if the aqua regia used be weak, and the contact with it is prolonged.

4. *Palladium, Iron, and Copper*.—The liquor charged with sal-ammoniac and alcohol, from which the platinum and iridium have been separated, is evaporated to get rid of the alcohol, and then treated with an excess of nitric acid, which transforms the ammonium chloride into nitrogen and hydrochloric acid. It is now evaporated almost to dryness. The residue is removed to a covered porcelain crucible, which is weighed with great care. When the matter is dry it is moistened with concentrated ammonium sulphide, and afterwards dusted over with 2 or 3 grammes of pure sulphur. When dry, this crucible is placed within a larger one of clay and surrounded with pieces of wood charcoal. The two are covered, and now set in a cold furnace, which is filled up with charcoal, and the fire is lighted at the top to avoid the projection of any matter from the crucible if it were too quickly heated. After reaching a bright red heat, the crucibles are allowed to cool. The porcelain crucible now contains palladium in a metallic state, with the iron and copper sulphides, and also the gold and rhodium. This mixture is moistened with concentrated nitric acid, which, after prolonged digestion at 70°, dissolves the palladium, iron, and copper, forming at the same time a little sulphuric acid. The solution of the nitrates is poured off the residue, which is washed by decantation, and the solution and washings are evaporated to dryness, and then calcined at a strong red heat. In this way the palladium is reduced, and the iron and copper pass to the state of oxides, which are easily separated from the palladium by means of strong hydrochloric acid. The palladium remains in the crucible, in which it is again strongly ignited and then weighed.

The iron and copper chlorides are now evaporated to dryness at a temperature but little above 100° C., and are then treated with ammonia. The iron sesquichloride, having lost nearly all its acid, has become insoluble; but the copper chloride is readily dissolved, and may be filtered from the iron, which is washed, ignited, and weighed. The copper solution is now evaporated almost to dryness, and then mixed with excess of nitric acid and heated to drive off the ammonium chloride. Afterwards the copper nitrate is ignited and weighed. The weight of the copper is always so small that the hygrometric water the copper oxide may absorb may be neglected.

5. *Gold and Platinum*.—The residue insoluble in nitric acid is weighed and treated with very dilute aqua regia, which takes up the gold, and sometimes, but very rarely, traces of platinum. To ascertain if platinum be present, evaporate to dryness, and redissolve by alcohol and ammonium chloride. If any platinum-yellow remain, it must be ignited and weighed. The difference in the weight of the porcelain crucible before and after the treatment by aqua regia gives the weight of the gold, from which, if any be found, the weight of the platinum must be deducted.

6. *Rhodium*.—The residue left in the crucible is rhodium, which must be reduced in a current of hydrogen.

Bunsen's Method of analysing platinum residues is as follows :—The residues employed contained no osmium, and were relatively rich in rhodium.

Platinum and Palladium.—It is easy to effect the almost complete separation of platinum and palladium from rhodium, iridium, and ruthenium. The original material is mixed in a Hessian crucible, with from $\frac{1}{2}$ to $\frac{3}{4}$ its weight of ammonium chloride, heated until the latter is completely volatilised, allowed to glow gently until only the vapours of iron sesquichloride show themselves, and then placed in a porcelain dish and evaporated to a syrupy consistency, with from 2 to 3 times its weight of crude nitric acid. By this treatment with ammonium chloride the metals present not belonging to the platinum group will have been partially converted to lower chlorides, the rhodium, iridium, and ruthenium will have been rendered insoluble, and the silica present as gangue converted from a gelatinous mass to a finely pulverulent condition, in which state it will admit of speedy filtering.

The chlorine compounds, produced by the ammonium chloride, give, upon digestion with nitric acid, just enough hydrochloric acid to dissolve the platinum to bichloride, while the metallic copper and iron present act so far reducingly upon the palladium (in solution in nitric acid) that it remains in solution, not as bichloride, but as the protochloride, which latter is not precipitated with potassium chloride. The mass is diluted with water, filtered, and the solution saturated with potassium chloride, and the greater part of the platinum separated pure as potassium platinochloride, which is washed out, first with potassium chloride, and later with absolute alcohol (the last washings must not be added to the solution).

The filtrate is brought into a large flask (which can be made airtight), which will not be more than half-filled with it. Chlorine gas is led into this flask, and it is, from time to time, shaken vigorously, until no further absorption of gas takes place, when all the palladium will have separated as a cinnabar-red precipitate of potassium palladichloride (somewhat impure, however, from traces of platinum, iridium, and rhodium). The fluid from which these precipitates were obtained is now evaporated, not quite to dryness, with hydrochloric acid; and, upon addition of just so much water as is necessary to dissolve out the potassium chloride and other soluble salts (aiding the operation by rubbing with a pestle), there remains behind a dirty, yellow-coloured precipitate. This is separated by filtration, boiled with caustic soda and a few drops of absolute alcohol. Hydrochloric acid is added to dissolve the precipitate formed, and the liquid then saturated with potassium chloride; the result is a precipitate of chemically

pure potassium platinochloride. The mother-liquid contains only copper and no platinum metals.

The purification of the cinnabar-red precipitate of palladium is accomplished as follows :—Dissolve in boiling water, whereby a portion of the chloride dissolves, with evolution of chlorine, to palladium protochloride. Then evaporate with $2\frac{1}{2}$ times its weight of oxalic acid, and dissolve again in a solution of potassium chloride ; whereupon potassium platinochloride remains behind, chemically pure. Wash out as before.

The brown liquid is then somewhat concentrated upon the water-bath ; and upon cooling, there separate bright green, well-formed crystals of potassium palladio-protochloride (with some potassium chloride), which, upon testing, proves free from the other platinum metals.

The fluid poured off from these crystals is then neutralised carefully with caustic soda, and gives a slight precipitate of copper and iron, which is filtered off. Upon adding potassium iodide to the filtrate, all the palladium separates as palladium iodide. To avoid adding an excess of the reagent, it is best to take, from time to time, a drop from the fluid with a capillary tube, and bring the same upon a watch-glass. As long as the precipitation is incomplete, the drop appears, upon a white background, *brown* ; when complete, it is *colourless* ; when the reagent is present in excess, it is *red*. This is tested for its purity by reducing it to metallic palladium, and then heating and dissolving in nitric acid ; when pure, it must dissolve completely. The whole mass is now reduced in a slow stream of hydrogen gas (whereby the iodine can be obtained again, as hydriodic acid, by absorbing with water). At last the mass must be strongly heated, to decompose slight traces of the palladium subiodide which are formed.

The mother-liquid from which all this platinum and palladium have been obtained may contain some iridium and rhodium ; it is, therefore, evaporated to dryness with a little potassium iodide, whereby a mixture of the rhodium and iridium iodides separates. This can either be dissolved in aqua regia and the two metals separated (as will hereafter be described) by sodium bisulphite, or it can be united with the next portion from which these metals will be obtained.

Ruthenium, Rhodium, and Iridium.—The residue from the original material which remains, after treatment with ammonium chloride and nitric acid, is treated as follows, to get the metals in a form adapted to further chemical treatment.

The method depends upon the behaviour of zinc chloride to zinc. If a piece of zinc be melted, it rapidly covers itself with a stratum of oxide. If to the melted metal a metal like iridium be added, the oxide stratum hinders the latter from coming into contact with the zinc, even though it be pushed beneath the surface. If, however, a

few grains of ammonium chloride be added to it, ammonia, hydrogen, and zinc chloride will be formed, which last dissolves the oxide stratum to basic zinc chloride. The zinc below resembles mercury in lustre and mobility. As soon as the chloride has dissolved as much of the oxide as is possible for it, the oxide stratum again forms, and is instantly removed again by the addition of more ammonium chloride. The melted zinc, strewn with ammonium chloride, also possesses, like mercury, the property of attacking other metals, if the affinity exists of forming with them alloys. By strewing ammonium chloride upon the melted zinc, a quiet surging is kept up, as the ammonia and hydrogen are given off. Many oxides and chlorides (among which are those of the platinum metals), when they come into contact with this atmosphere of reducing gases, and with the basic zinc chloride, are instantly reduced and dissolved by the zinc. In making the solution, the zinc, in a porcelain dish, should be constantly rotated: the gangue remains in the basic chloride. The regulus, immediately upon solidifying, should be taken from the capsule, out of the yet-fluid basic chloride, and washed off with acetic acid until all the basic chloride is dissolved away. The gangue can be quantitatively estimated by filtration and weighing. If the regulus is not immediately removed, the containing vessel will be broken, owing to the unequal expansion of the porcelain and the metal.

The best proportions for a quantitative separation are, to 1 part of the platinum metals, from 20 to 80 parts of zinc. For an ordinary separation, 7 parts of zinc are sufficient.

For the extraction of the residues remaining after the treatment with nitric acid this method is admirably adapted. By fusing only once with zinc for 2 or 8 hours, all the platinum metals are extracted. The operation is the following:—

From 8 to 8.5 kilogrammes of commercial zinc are fused in a 2-litre Hessian crucible, ammonium chloride from time to time strewn upon it; 400 grammes of residue, previously heated to faint glowing with ammonium chloride, are added, and the temperature kept, for 2 or 8 hours, just above the fusing-point of the alloy, by adding, whenever the mass threatens to solidify, some ammonium chloride. The mass is divided into three strata after solidification has taken place.

The outer stratum, easily broken away by a blow from a hammer, contains no platinum metals. The next contains some particles of the zinc and platinum alloy, imbedded in the basic zinc chloride; it is porous, and not very thick. The inner stratum consists of a beautiful crystalline regulus.

To obtain the alloy from the middle stratum, it is only necessary to wash repeatedly with water; and the alloy gained is, of course, to be added to the regulus. To obtain this regulus as pure as possible, it is again fused with 500 grammes of zinc and some ammonium chloride, then granulated in water, and the granules dissolved in

fuming hydrochloric acid. The acid attacks the regulus with the greatest energy, and the solution is complete in less than an hour. The zinc chloride can be used for the next operation.

The platinum metals are found at the bottom of the vessel, in the form of a finely-divided black powder, which is contaminated with zinc, and with traces of iron, copper, &c. from the latter. It cannot be purified with nitric acid, nor with aqua regia, for part of the platinum metals will thereby be dissolved, or, at best, so suspended in the fluid that filtration is impossible. If, however, the powder is treated with hydrochloric acid, singularly enough, all the impurities are dissolved; not only zinc and iron, but also lead and copper, dissolve readily, with the generation of hydrogen. The explanation is readily found in electrical currents produced by the contact of the metals, the stream passing from the positive zinc, iron, &c. to the negative platinum metals, hydrogen being given off on the latter and chlorine on the former, and uniting with them. The metallic powder, after thorough washing, possesses the property, upon being gently heated, of exploding weakly, and, when highly heated, with violence, the explosion being accompanied with the evolution of light; thereby neither hydrogen, nor chlorine, nor nitrogen, nor aqueous vapour are given off; and, as these are the only elements which it is possible that the metallic powder could have taken up, it must be assumed these metals are, by this treatment, converted into an allotropic condition, and that, upon heating, they return, with more or less energy, to their original condition. The powder contains, mainly, rhodium and iridium; but there are traces present of platinum, palladium, lead, copper, iron, and zinc.

It is intimately mixed with about 3 or 4 times its weight of completely anhydrous barium chloride, and a stream of chlorine gas led over it at a tolerably high temperature. The operation is concluded when particles of iron sesquichloride show themselves on the neck of the flasks containing the powder. These are carefully brushed away with filter-paper. Some water is now added, and the mass of the platinum metals dissolved with the evolution of heat. There remains behind insoluble matter, which, upon reduction with hydrogen, alloying with zinc, and treatment with hydrochloric acid, furnishes ruthenium. From the solution all the barium chloride is removed by careful addition of sulphuric acid. The platinum metals are now completely freed from all other metals by reduction with hydrogen, the temperature being, throughout the operation, maintained at nearly 100° C., by means of a constant water-bath. Platinum and palladium chiefly separate first; then mainly rhodium; and the last portions consist almost entirely of iridium. It is best to break off the operation when the fluid has assumed a greenish-yellow colour. The last portions of iridium (obtained by evaporating the solution to dryness, fusing with sodium carbonate, and treatment with aqua regia) are

added to the portion, afterwards to be again rendered workable by renewed treatment with barium chloride. The operation of reduction is hastened by concentrating the fluid, in doing which care must be taken to guard against explosion, on account of the hydrogen. The separated metals are treated with aqua regia, and the platinum and palladium thus dissolved separated from each other, as already described. The traces of rhodium and iridium in the mother-liquid can be removed entirely by continued boiling with potassium iodide (whereby they are precipitated as iodides); they are then dissolved in aqua regia and added to the insoluble portion.

This insoluble and partly oxidised portion is now again reduced in hydrogen gas, treated, as before described, with barium chloride, and, after the removal of the barium, the last traces of platinum and palladium removed by boiling with caustic soda. Rhodium and iridium now alone remain to be separated.

The brown-red fluid is, for this purpose, evaporated with hydrochloric acid, and, after filtration, treated with sodium bisulphite in great excess, and the whole allowed to remain quietly in the cold for several days. The double rhodium and sodium sulphide separates slowly, giving a lemon-yellow precipitate. The solution becomes lighter and lighter, and finally almost colourless. The colour of the precipitate changes with that of the fluid, becoming, with it, lighter. This precipitate, upon washing, contains the rhodium almost pure.

Upon heating the fluid gently, a yellow-white precipitate separates, which consists mainly of rhodium, but contains, also, some iridium. After filtering off this precipitate, the solution, upon being concentrated to a small volume, gives yet two precipitates—

1. A curdy, slowly separating, yellowish-white precipitate, containing nearly chemically pure iridium, with but the faintest traces of rhodium.

2. A heavy, crystalline powder, quickly separating, which is readily freed from the first by decantation. Upon testing, it gives all the reactions for iridium, but likewise some peculiar reactions not shown by the latter. It may possibly contain a new metal.

The complete separation of rhodium from iridium is accomplished by treating the yellow precipitates with concentrated sulphuric acid. They are brought in small portions into the acid, heated in a porcelain capsule until all the sulphurous acid has escaped, and then left upon the sand-bath until the free sulphuric acid has been driven off and the sodium sulphate formed. Upon boiling the mass in water, all the iridium dissolves as sulphate, with a chrome-green colour; while the rhodium remains behind as a flesh-coloured double sodium and rhodium salt. The latter is boiled in aqua regia, and washed by decantation. It is insoluble in water, hydrochloric or nitric acids, and in aqua regia. The rhodium and iridium are now completely separated.

The first yellow precipitate obtained in the cold by the sodium

bisulphate gives, by this treatment, the rhodium quite pure. The second and third precipitates, containing much iridium, give a very fine rhodium, but still slightly contaminated with iridium. The products, therefore, obtained by this treatment with sulphuric acid (which betray their contamination with iridium by their somewhat brownish colour) are collected for themselves, the rhodium separated therefrom by glowing, treated again with barium chloride, and the operation of separation repeated. The green solution, containing only iridium, is gradually heated over an ordinary burner, in a porcelain capsule, and, afterwards, upon the sand-bath, to remove the excess of sulphuric acid; and, finally, the capsule and its contents are highly heated in a Hessian crucible. There are formed thereby sodium sulphate and iridium sesquioxide. Upon boiling the mass with water, the last remains behind as a black, insoluble powder, which is readily washed by decantation.

C. Lea's Process for Analysing Platinum Ores.—The ores on which these analyses were performed contained chiefly iridium, together with ruthenium, osmium, rhodium, and platinum. It was a Californian osmiridium which had already undergone a preliminary fusion with nitre and caustic potash.

This material is boiled with aqua regia to extract all the soluble portions, the residue then ignited with nitre and caustic soda,¹ and the fused mass heated with water. From the resulting solution small portions of potash osmite crystallise out. The metallic oxides are next precipitated, and this precipitate, together with the portions insoluble in water, is boiled again with aqua regia, ignited, &c. These ignitions still leave a small portion of unattacked residue.

The boiling with aqua regia is continued for a long time, in order to get rid as thoroughly as possible of the osmic acid. Even after 200 hours' boiling, osmium is still left in the solution in easily recognisable but comparatively small quantity. The greatest advantage is found throughout the whole of this part of the operation from the use of a blowing apparatus, with the aid of which all inconvenience from the fumes of osmic acid is avoided. The apparatus is constantly swept clear by a powerful air current, and the osmic acid is removed as fast as it is volatilised. As the ignition of the ore with alkaline nitrate and caustic alkali scarcely drives off any osmium, and as almost all inconvenience in manipulating the resulting solutions can be avoided by throwing down the metals with alcohol from the hot alkaline solution, in place of using acid, it is clear that the difficulties arising from the noxious effects of osmic acid can be almost wholly removed from each of the various stages of the process.

¹ Attention is necessary to the order in which these substances are employed. If the caustic soda is melted first, it attacks the iron vessel strongly, and may even go through. If added last it causes sudden and violent effervescence, with danger of boiling over. Therefore, place the nitre first in the vessel, and when it is fused add the caustic soda. When a red heat is obtained add the osmiridium by degrees.

A very prolonged treatment with aqua regia is found to have the great advantage of converting nearly the whole of the ruthenium into bichloride. The separation of ruthenium in this form from the other metals is so easy in comparison with the difficulties presented by the separation of the sesquichloride, that this advantage cannot be looked upon as other than a very material one.

Sal-ammoniac is next added to the mixed solution in quantity sufficient to saturate it. The sandy crystalline precipitate (A) is thoroughly washed out, first with saturated and then with dilute sal-ammoniac solution. The saturated solution of ammonium salt carries through with it nearly the whole of the ruthenium as bichloride (B); the dilute solution is found to contain small quantities of iridium, rhodium, and ruthenium (C).

Over (A), water acidulated with hydrochloric acid is placed, and allowed to stand for some days. This is treated with ammonia and boiled. The precipitate, when treated with hydrochloric acid, furnishes green osmium chloride, with traces of ruthenium.

In these preliminary steps Claus's process has been followed, which undoubtedly offers advantages over any other, and best brings the metals into a convenient state for separation, varying it only by prolonging the treatment with aqua regia, and converting the ruthenium principally into bichloride instead of sesquichloride.

We have now 8 portions of material :—(A), consisting of ammonium iridiochloride, containing also ruthenium, osmium, rhodium, and platinum in small quantities. (The ore under examination contained no palladium, which metal, if present, has always its own peculiar mode of separation, and does not enhance the difficulties of operation.) (B), containing ruthenium bichloride, together with iron in quantity, copper, and other base metals which may be present. Finally, (C), containing chiefly ruthenium bichloride, mixed with small quantities of iridium and rhodium.

The next step in the process is to introduce the ammonium iridiochloride (A) into a large flask with 20 to 25 times its weight of water, and apply heat until the solution is brought to the boiling-point; the whole of the ammonium iridiochloride should be brought into solution in order that the reduction to be effected may not occupy too long a time, as otherwise the platinum and ruthenium salt, if any be present, might likewise be attacked. Crystals of oxalic acid are thrown in as soon as the solution actually boils, whereupon a lively effervescence takes place, and the iridium salt is rapidly reduced. As fast as the effervescence subsides, more oxalic acid is added, until further additions cease to produce any effect. When this is the case, the liquid is allowed to boil for 2 or 3 minutes longer, not more; the heat is to be removed, and the flask plunged into cold water.

By this treatment any platinum present is unaffected. Sal-ammoniac in crystals is added, about half enough to saturate the quantity

of water present. The sal-ammoniac may be added immediately before the flask is removed from the fire. After cooling, the solution should be left for a few days in a shallow basin, whereby the ammonium platinochloride will separate out as a yellow, a reddish, or even (especially if the quantity of water used was insufficient) as a black crystalline powder, according to the quantity of iridium which it may contain.

The mother-liquor is to be again placed in a flask and boiled with aqua regia. On cooling, the ammonium iridiochloride crystallises out, and any traces of rhodium and ruthenium which may be present remain in solution. The iridium salt is to be washed with a mixture of 2 parts saturated solution of sal-ammoniac and 3 parts of water, and may then be regarded as pure.

The treatment by oxalic acid affords iridium free from all traces of ruthenium. The detection of very small quantities of ruthenium in presence of much iridium has been hitherto an impossibility, or could only be effected by Claus's method of allowing a small quantity of water acidulated by hydrochloric acid to remain in contact with the ammonium iridiochloride for some days. The ruthenium salt, by its superior solubility, tended to dissolve first; hence the acidulated water, after standing, contained ruthenium in larger relative proportion than the original crystals; the ruthenium reactions were more marked, and if it was present, and in sufficient quantity, it could be detected by potassium sulphocyanide, or, better, to an experienced eye, by lead acetate. The objections to this method are sufficiently obvious.

The treatment of solutions (b) and (c) presents no difficulty. With (b) the best plan is to place the solution aside in a beaker covered with filter-paper for some time. Treated in this way, the bichloride gradually crystallises out, and by recrystallisations may be obtained in a state of perfect purity.

Solution (c) is to be evaporated to dryness, and reduced to an impalpable powder. It is then to be thrown upon a filter, and thoroughly washed with a perfectly saturated solution of sal-ammoniac. The ruthenium bichloride is thus carried through, with perhaps a trace of rhodium sesquichloride, from which, however, it is easily freed by crystallisation. From the residue, the rhodium and ammonium sesquichloride is removed by a dilute solution of sal-ammoniac, perfectly free from the iridium, which is left behind.

In connection with this separation, Mr. Lea makes a remark which, though of special reference to this particular case, is also applicable to all those cases in which the double chlorides of the platinum metals are to be separated by their various solubilities in solution of sal-ammoniac. This most valuable process, for which we are indebted, as for so much else, to Claus, whose untiring labours have made him the father of this department of chemistry, requires to be applied with some attention to minutiae.

The crystalline matter must be reduced to the finest powder, and after being thrown upon the filter, it must be washed continuously until the separation is effected. Any interruption of the washing is followed by more or less crystallisation of sal-ammoniac through the material, which precludes an effectual separation. The same material which in a state of coarse powder will hardly yield up enough ruthenium bichloride to colour the sal-ammoniac solution, will, when thoroughly pulverised, give an almost opaque blood-red filtrate.

Solution (c) may be subjected to a different treatment from the foregoing, and oxalic acid may be used to effect the separation. The solution is to be brought to the boiling-point, and oxalic acid added as long as effervescence is produced. The iridium bichloride is thereby reduced, the ruthenium bichloride and the rhodium sesquichloride are not affected. Sal-ammoniac is then to be dissolved in the solution to thorough saturation. By standing and repose the double rhodium and ammonium chloride separates out. The solution is then reoxidised by boiling with aqua regia; by standing for some days in a cool place, the ammonium iridiochloride crystallises out, and the supernatant solution contains the double ammonium chloride and ruthenium bichloride, which may be rendered pure by several recrystallisations.

For purifying the double iridium and ammonium chloride, the oxalic process is decidedly the best. It is simpler and easier, and there is the further advantage that the platinum is left in the condition of double chloride, whereas when the usual method of treating with aqueous sulphuretted hydrogen is used, the platinum is apt to be converted partly into sulphide, together with any traces of rhodium and ruthenium which may be present. When oxalic acid is used, the platinum remains behind as a reddish powder, containing some iridium, from which it may be freed in the ordinary manner, if it is present in quantity sufficient to be worth working.

For treating a mixture such as that which is here designated as (c), containing no platinum, and only ruthenium present in the form of ammonium rutheniochloride, it is unnecessary to apply reducing agents, and the first method described is the best. But if it be proposed to effect the separation by the reduction of the iridium compound, the method here described is preferable to that based on the use of sulphuretted hydrogen even in this case.

The action of oxalic acid on the platinum metals is interesting; its reducing effect upon iridium bichloride at the boiling-point is immediate. On ruthenium bichloride it seems to have no effect whatever, and they may be boiled together for a length of time without sensible result. In a trial made with ruthenium and ammonium sesquichloride, the oxalic acid was boiled with the metallic salt for a considerable time without any apparent effect becoming visible, but by long-continued boiling a gradual precipitation took place. When ammonium platinochloride was boiled with oxalic acid, no effect was produced for a con-

siderable time, but gradually the platinum salt diminished in quantity, and the liquid acquired a stronger yellow colour, perhaps owing to formation of soluble platinic oxalate. This process will not, however, furnish an easy and convenient method of purifying commercial platinum from the iridium always found in it, as the reduction of very small quantities of double iridium and ammonium chloride in the presence of a large proportion of the corresponding platinum salt is difficult and slow, and the platinum salt itself is evidently attacked.

Dr. Wolcott Gibbs's Process for the analysis of platinum ore is as follows:—The metals are first obtained in a nitrohydrochloric solution, and the liquid is then evaporated to dryness with an excess of sodium chloride. The mass of double chlorides obtained as already mentioned is to be rubbed to a fine powder, introduced into a deep porcelain evaporating-dish, and mixed with 4 or 5 times its volume of boiling water. A solution of sodium nitrate is then to be added in small quantities at a time, the solution being continually stirred, and occasionally neutralised by addition of sodium carbonate. The liquid soon becomes olive-green, and the greater part of the mass dissolves; it is advantageous, when the quantity of the mixed chlorides is large, to pour off the liquid as soon as it appears saturated, and to repeat the operation with a fresh quantity of water. The undissolved mass, which consists chiefly of the impurities of the ore, when these have not been removed before the process of oxidation, is then to be thrown upon a filter and washed with boiling water until the washings are colourless. By keeping the solution somewhat alkaline, the whole of the iron remains upon the filter as sesquioxide, with other impurities. The filtrate contains iridium and rhodium as sesquichlorides, ruthenium partly as bichloride and partly as protochloride, platinum as bichloride. When the operations already mentioned have been well performed, no determinable quantities of osmium and palladium are present. On cooling, the greater part of the platinum is deposited as potassium platinochloride mixed with a little of the corresponding iridium salt, and is to be separated by pouring off the olive-green supernatant liquid. The quantity of the alkaline nitrite to be added in this process need not exceed half of the weight of the mass of double chlorides, but with a little experience it will be found unnecessary to weigh the nitrite added, the process of the reduction of the potassium iridiochloride being evident to the eye.

To the filtrate a solution of sodium nitrite is to be added, and the whole boiled until the liquid assumes a clear orange-colour. Sodium nitrite should be used in this process, because the resulting double iridium and sodium nitrite is easily decomposed by boiling with hydrochloric acid, which is not the case with the potassium salt. When potassium nitrite is used, a small quantity of the white insoluble double salt already mentioned is usually formed and renders the solution turbid.

To the clear yellow, or orange-yellow, boiling solution, sodium sulphide is to be added until a portion of the dark brown precipitate of the ruthenium, rhodium, and platinum sulphides is dissolved with a brown-yellow colour, and an excess of the alkaline sulphide is, consequently, present. The liquid is then to be allowed to cool, and treated with dilute hydrochloric acid, until a distinctly acid reaction is produced. In this manner the whole of the platinum, ruthenium, and rhodium present in the solution are thrown down as insoluble sulphides. After complete subsidence, the sulphides are to be thrown on a double filter and thoroughly and continuously washed with boiling water. When the operation is carefully performed, the filtrate and washings contain only iridium. It is best to neutralise this solution with sodium carbonate, boil a second time with a little additional sodium nitrite, and treat as before with sodium sulphide and hydrochloric acid. In this manner very small additional quantities of the platinum, ruthenium, and rhodium sulphides may sometimes be separated.

The filtrate is to be evaporated and boiled with an excess of strong hydrochloric acid, which completely decomposes the double iridium and sodium nitrite, yielding the sodium iridiochloride, which is very soluble in water. An excess of a pure and strong solution of ammonium chloride is then to be added, the whole evaporated to dryness, and the dry mass washed with cold water, and then with a cold and strong solution of sal-ammoniac. There remains a mass of pure ammonium iridiochloride, which may be advantageously rubbed to a fine powder, dissolved in boiling water, and allowed to crystallise. The resulting salt is chemically pure, and the crystals possess an extraordinary beauty and lustre. The mass of mixed sulphides, together with the filter, are to be treated with strong hydrochloric acid, and nitric acid added in small portions at a time. By the aid of a gentle heat the sulphides are readily oxidised and dissolved. After sufficient dilution, the liquid is to be filtered, the pulp of undestroyed filter-paper washed, the filtrate evaporated to dryness, the dry mass digested with concentrated hydrochloric acid, and again evaporated to dryness. The dry mass of chlorides and sulphates is to be redissolved in water, and the platinum, ruthenium, and rhodium precipitated by metallic zinc, after addition of hydrochloric acid. The finely divided metals, after filtration, washing, and drying, are then to be mixed with potassium chloride, and treated with dry chlorine at a low red heat. In this manner the metals are again brought into the form of double chlorides, and the difficulties which arise from the presence of the sulphates are avoided.

The mixed double chlorides are to be boiled with potassium nitrite, evaporated to dryness, and the soluble ruthenium and potassium nitrites dissolved out with absolute alcohol in the manner described in speaking of the separation of platinum from ruthenium (page 474). The

ruthenium may then be obtained pure by converting it into the double mercury and ruthen-diamine chloride (page 475).

The mass undissolved by alcohol consists of potassium platino-chloride mixed with both the soluble and the insoluble double rhodium and potassium nitrites. It is to be boiled with dilute hydrochloric acid, neutralised with potassium carbonate, again evaporated to dryness, after the addition of potassium nitrite, and again boiled with absolute alcohol, which sometimes dissolves a trace of ruthenium. The undissolved mass is then to be treated with hot water, and again evaporated to dryness, and this process repeated two or three times, so as to convert the whole of the soluble rhodium salt into the insoluble salt. The potassium platinochloride may then, after reducing the mass to fine powder, be dissolved out by boiling water, when the rhodium salt remains pure, as a fine orange-yellow crystalline powder. This may be dissolved in hot hydrochloric acid, evaporated to dryness with an excess of pure ammonium chloride, and ignited in a clean porcelain crucible, when pure metallic rhodium remains as a porous mass mixed with potassium chloride.

When the process above described has been carefully conducted, and especially when the quantity of sodium nitrite added is sufficient, the mixed sulphides will be found to contain only platinum, rhodium, and ruthenium, and to be free from iridium. If, however, after converting the sulphides into double chlorides in the manner pointed out, iridium is found to be present, the process to be pursued is still the same so far as regards the separation of the ruthenium; the remaining mass is then to be dissolved in water with addition of hydrochloric acid, the solution nearly neutralised with ammonia, the platinum and rhodium separated as sulphides in the manner already pointed out, brought into the form of double chlorides, and then separated by potassium nitrite as before.

For the complete success of this method it is absolutely necessary that the mass of mixed double chlorides be freed from osmium as completely as possible. This may be done in the usual manner by repeated evaporation with nitro-hydrochloric acid.

Preparation of Platinum Chloride from Residues.

The concentrated alcoholic solutions are reduced, at a boiling temperature, by a mixture of soda solution and glycerine or sugar. Platinopotassic chloride is also completely reduced if gradually added to the boiling mixture, and if sufficient soda is present. The precipitate of platinum black is washed by decantation in a porcelain capsule till all the sulphuric acid and potassium are eliminated, dried, ignited and digested at a gentle heat in hydrochloric acid to extract iron, &c., and then sufficient nitric acid is gradually added. The solution is evaporated down at a gentle heat; the platinous chloride is converted into platinic chloride by the addition of fuming hydrochloric

acid and a little nitric acid; the excess of the latter is expelled by the repeated addition of water and hydrochloric acid, and evaporation. The presence of platinous chloride is detrimental for the estimation of potassium, rendering the results too high, whilst nitric acid occasions an error in the contrary direction. Traces of iridium have little effect on the accuracy of the analysis. The solubility of platino-potassic chloride in alcohol is 1 part in 42,600 absolute, 1 part in 37,800 at 96 per cent., and 1 in 26,400 at 80 per cent. Platino-sodic chloride is soluble in boiling water in almost every proportion. Platino-baric chloride has the important property of being more or less completely decomposed into platinum chloride and barium chloride.

Mending Platinum Crucibles.—Mr. T. Garoide gives the following simple method :—Some months ago I had a platinum dish, which had a small hole on the side, near the bottom, and the dish was consequently useless for most purposes. I was about to consign it to the old platinum, when it struck me that this metal being 'weldable' I might manage to repair it. Having already a mould for this dish, made of plaster-of-Paris, and not of wood, this served admirably as an anvil. I then cut a piece of moderately thin platinum foil, about 8 millimetres diameter, and rubbed this and the part of the dish where the hole was with sea-sand until perfectly bright and clean. Having fixed the dish and its mould in an upright position, I laid the platinum foil over the hole, and directed the flame from a table blowpipe upon the spot. A pair of scissors served as a hammer, and by gently tapping with these the two pieces of platinum united perfectly, and made so neat a joint that one would scarcely observe it unless one's attention was called to it. I have used the dish for all kinds of purposes since, but the union is as good as ever. In the above operation the plaster-of-Paris mould, although very dry, was split and cracked by the heat in all directions, nevertheless it had sufficient cohesion to last until the operation was concluded. I find that platinum wires are very easily joined in this way.

PALLADIUM.

Test for the Presence of Palladium.

Carey Lea proposes sodium thiosulphate as a delicate test for many of the platinum metals. For detecting the presence of palladium he proceeds as follows :—Place a solution of sodium thiosulphate in a test-tube with a little liquid ammonia, and add a drop of the palladium solution, so that it shall communicate a pale lemon colour only to the liquid. By boiling, this rapidly darkens to a wine-brown shade, increasing in intensity until it finally appears black. Dilution, however, shows that this results from its intensity only; the diluted liquid is free from turbidity and has a warm-brown tint.

Separation of Palladium from Copper.

Saturate the solution containing these metals with sulphurous acid gas and add a solution of potassium sulphocyanide. This has no action on the palladium, whilst it completely precipitates the copper in the form of a white sub-sulphocyanide.

RHODIUM.

Separation of Rhodium from Platinum.

The usual method of approximately separating these metals is, to convert them into their potassium or ammonium double chlorides, and then to carefully wash out the rhodium salt by small successive portions of cold water, or, better, by a moderately concentrated solution of potassium or ammonium chloride. By recrystallising the platinum and rhodium salts respectively, they may be obtained in a state of purity, since they are not isomorphous.

To obtain rhodium absolutely free from platinum, Dr. Wolcott Gibbs advises to convert the two metals into the ammonium double chlorides, separate the rhodium salt as completely as possible by washing with a solution of sal-ammoniac, and then evaporate the double rhodium and ammonium chloride with a solution of ammonia. In this manner the rhodium is converted into the chloride of the ammonia-rhodium base, discovered by Claus, while the platinum forms no well-defined or crystallisable compound. The chloride of Claus's base may then be purified by repeated crystallisation.

IRIDIUM.

Separation of Iridium from Platinum.

The following process for separating these metals was proposed by Dr. Wolcott Gibbs:—The iridium is, in the first place, to be brought into the form of bichloride, by means of a current of chlorine or by nitric acid, and the two metals are then to be precipitated together as potassium double chlorides, by the addition of a concentrated solution of potassium chloride. The colour of the mixed salts varies from orange to almost black, according to the quantity of iridium present. The mass of crystals is to be rubbed fine in an unglazed porcelain mortar, and boiling water added in the proportion of three volumes of water to one of salt. A dilute solution of potassium nitrite is then to be added until the liquid becomes deep olive-green, sodium carbonate being thrown in from time to time in quantity sufficient to prevent the solution from becoming strongly acid. The iridium is instantly reduced to sesquichloride, while the platinum salt remains as a reddish-orange powder. The deep olive-green solution is to be poured off, and the undissolved mass treated a second time with hot water and nitrite. This process must be repeated as long as the liquid remains olive-green. The mixed solutions on cooling, or after evaporation, deposit

a beautiful mass of crystals of the double potassium chloride and iridium sesquichloride. By re-solution and repeated crystallisation, the iridium salt may be obtained perfectly free from platinum. The undissolved mass and the mother-liquors from the iridium salt contain a large quantity of platinum with a comparatively small quantity of iridium. When the absolute quantity of platinum salt is not very large, it may be dissolved in boiling water, a small quantity of alkaline nitrite added, and the solution allowed to crystallise; the resulting potassium chloroplatinate contains only a trace of iridium.

This process gives satisfactory results when carefully executed, but requires attention to two points. In the first place the alkaline nitrite must be added in quantity just sufficient to reduce the iridium from bichloride to sesquichloride, but not so as to produce further chemical changes by the formation of the double iridium and potassium nitrite or sodium; with a very little experience this is easily managed. In consequence of the facility with which the double iridium and sodium nitrite is decomposed by boiling with hydrochloric acid into the double chloride, $\text{IrCl}_2 \cdot 2\text{NaCl}$, it is better to use sodium nitrite in the above process, because, in case an excess of nitrite is used, the mixed solution of double chloride and double nitrite can easily be brought to the form of the double chloride, $\text{Ir}_2\text{Cl}_3 \cdot 8\text{NaCl}$, by boiling with hydrochloric acid, neutralising with sodium carbonate, and then reducing the iridium to sesquichloride by cautiously adding a very dilute solution of sodium nitrite.

In the second place, it may happen, as in working with crude platinum solutions obtained not from osm-iridium but from platinum ores, that the quantity of platinum is very large when compared with that of iridium. The process applies equally well to this case as far as the iridium is concerned, but it is difficult and troublesome to re-crystallise large quantities of a salt so insoluble as potassium platinochloride, and small quantities of the corresponding iridium salt are difficult to remove.

The following process can be recommended for giving chemically pure iridium when platinum is the only other metal present:—The greater portion of the platinum is first to be separated in the manner above pointed out. The solution of double iridium and sodium chloride, $\text{Ir}_2\text{Cl}_3 \cdot 8\text{NaCl}$, is then to be filtered, an excess of sodium nitrite added, and the solution boiled until it assumes a clear orange-yellow colour. To the boiling solution sodium sulphide is added drop by drop as long as this produces a cloudiness, and until a small quantity of the precipitated platinum sulphide is redissolved. Dilute hydrochloric acid is then to be added cautiously until the liquid, previously allowed to become cold, is distinctly though faintly acid, when it is to be filtered and the platinum sulphide in the filter washed continuously with hot water. The filtrate is then to be boiled with hydrochloric acid in excess, and the resulting sodium iridiochloride evaporated, pre-

precipitated by a cold and strong solution of sal-ammoniac, and washed with the same. This salt, on ignition, yields pure iridium if the operation has been well conducted. It is, however, in all cases well, after separating the platinum sulphide by filtration, to neutralise the filtrate with sodium carbonate, boil a second time with a little additional sodium nitrite, and then add sodium sulphide and proceed as before. In this manner every trace of platinum is removed, and the resulting iridium salt is chemically pure.

Separation of Iridium from Rhodium.

Iridium may be approximately separated from rhodium by the process recommended by Claus, which consists in taking advantage of the solubility of the double rhodium and ammonium chloride, $\text{Rh}_2\text{Cl}_3 \cdot 8\text{NH}_4\text{Cl}$, in moderately strong solutions of ammonium chloride, in which the ammonium iridochloride is nearly insoluble. This method is difficult of application when the quantity of rhodium is small, and is at best tedious and unsatisfactory. A better method is the following:—To the solution containing the two metals, sodium nitrite is to be added in excess, together with a sufficient quantity of sodium carbonate to keep the liquid neutral or alkaline; the whole is then to be boiled until the solution assumes a clear orange-yellow or orange colour. If a green tint should be perceptible, more sodium nitrite must be added and the solution again boiled. Both iridium and rhodium are converted into soluble double nitrites. A solution of sodium sulphide is then to be added in slight excess, the liquid rendered slightly acid, filtered, and the dark brown rhodium sulphide thoroughly washed. The filtrate is perfectly free from rhodium. This is boiled with excess of hydrochloric acid, evaporated, precipitated with sal-ammoniac, and treated as described in the method of preparing pure iridium given above. The rhodium sulphide, together with the filter, is to be treated with strong hydrochloric acid, and sal-ammoniac added in quantity sufficient to form ammonium rhodochloride. Nitric acid is to be added from time to time in small quantities, until, with the aid of heat, the whole of the rhodium sulphide is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salts with a strong solution of sal-ammoniac, the double rhodium and ammonium chloride, $\text{Rh}_2\text{Cl}_3 \cdot \text{NH}_4\text{Cl}$, is left behind. This is insoluble in a cold saturated solution of sal-ammoniac, in which it may be washed once or twice to remove alkaline salts and any traces of iridium which may be present as sulphate. The rhodium salt is then to be purified by crystallisation, or converted into the chloride of Claus's rhodium-ammonium base by evaporation on a water-bath with a solution of ammonia. Iridium sulphate does not give a basic compound under these circumstances. The chloride, $5\text{NH}_3 \cdot \text{Rh}_2\text{Cl}_3$, is then to be further purified by crystallisation.

OSMIUM.

Reduction of Osmic Acid.

A solution of osmic acid on addition of potassium nitrite is reduced to osmious acid, which unites with the alkali, forming the well-known beautiful red salt. The solution may be evaporated to dryness without decomposition. The nitrite may, therefore, be added with great advantage when solutions containing free osmic acid are to be evaporated, or even transferred from one vessel to another. No other reducing agent answers the same purpose, as the osmium is obtained at once in a very convenient form for preservation. When a solution of osmic acid, to which potassium nitrite has been added, is evaporated sufficiently and then allowed to cool, beautiful garnet-red octahedral crystals of potassium osmite separate.

These should be dried over sulphuric acid, and not in contact with paper or organic matter, which partly reduces the osmious acid to the brown osmium sesquioxide. Potassium nitrite exerts no sensible action when boiled with a solution of potassium osmiochloride; any salt which may be formed is very soluble in water.

Separation of Osmium from Iridium (Analysis of Osm-Iridium).

Wöhler's Method of resolving osm-iridium consists in passing moist chlorine over the ore mixed with common salt and heated to low redness in a glass or porcelain tube. This method is invaluable in analysis, and gives excellent results in working the ore upon a small scale. In all cases, however, several repetitions of the process are necessary for complete resolution or reduction to a soluble form. On the other hand, it can scarcely be doubted that this method could be advantageously employed upon the large scale, if vessels of porcelain of large size and of a proper shape could be obtained. Such vessels might be constructed in the form of long and flattened ellipsoids, furnished at each extremity with wide tubes several inches in length, and would be of great utility in various chemical processes. No process of fusion with oxidising agents compares with Wöhler's method in point of elegance, as no iron or other impurities afterward to be removed are introduced by the process itself.

Fritzsche and Struve's Process is to treat the ore with a mixture of equal parts of potassium hydrate and chlorate, by which a more or less complete oxidation is effected, without any sensible evolution of osmic acid. The temperature required in this process is not high, but large vessels must be employed, as the mixture froths very much at first. This process does not appear to possess any sensible advantage over that of Claus, which is, moreover, less expensive, and can be carried out with smaller vessels.

Claus's Method of resolving the ore consists in fusing for an hour, at a red heat, a mixture of 1 part of ore with 1 part of caustic potash and 2 of saltpetre. The fused mass is to be poured out upon a stone, allowed to cool, broken into small pieces or powdered, and then introduced into a flask, which is to be filled with cold water and allowed to stand for 24 hours. The clear deep orange-red solution of potassium osmiate and rutheniate is then to be drawn off by means of a syphon, and the black mass remaining again washed in the same manner. The finely divided oxidised portion of the insoluble matter may now be separated from the unattacked ore by diffusion in water and pouring off, after the subsidence of the heavier ore. The unattacked ore is then to be fused a second time with potash and saltpetre and treated as before. Claus asserts that he has been able in this manner to resolve the Siberian osm-iridium completely in two operations.

Dr. Wolcott Gibbs, to whom the chemistry of the platinum metals is so greatly indebted, recommends the following process for the analysis of osm-iridium:—The ore, which is usually very impure, is in the first place to be fused with 8 times its weight of dry sodium carbonate. The fused mass after cooling is to be treated with hot water, to remove all the soluble portions, and then the lighter portions are to be separated by washing from the heavy unattacked ore. In this manner the greater part of the silica and other impurities present may be removed. A previous purification of this kind is not indispensable, and may be omitted altogether when the ore is in plates or large grains, but it is very desirable when the ore is in fine powder, and greatly facilitates the subsequent action of the oxidising mixture. By cutting off the top of a mercury bottle a wrought-iron crucible is obtained, in which 600 grammes of osm-iridium may be fused at one operation with potash and saltpetre as above. There is usually little or no foaming, and if any occur it may easily be checked by stirring with an iron rod. No sensible quantity of osmic acid is given off during the process, which with a little care is entirely free from danger. In this manner 1500 grammes of ore have been worked up in a few hours in three successive operations. The fused mass is to be broken into pieces with a hammer, and brought into a clean iron pot. Boiling water, containing about $\frac{1}{10}$ of its volume of strong alcohol, is then to be added, and the whole is to be boiled over an open fire until the fused mass is completely disintegrated. The potassium osmiate is, in this manner, reduced to osmite, while the potassium rutheniate is completely decomposed, the ruthenium being precipitated as a black powder. It is advantageous, after boiling for some time, to pour off the supernatant liquid with the lighter portions of the oxides, and boil a second time with a fresh mixture of alcohol and water. In this manner we obtain a solution of potassium osmite, a large quantity of black oxides, and a heavy black and coarse powder. This last consists chiefly of un-

decomposed ore, mixed with a small quantity of the iridium oxides, &c., with scales of iron oxide from the crucible, and, if the ore has not been previously purified, with the impurities of the ore itself. The greater specific gravity of this residual mass renders it very easy to pour off from it the mixture of black oxides with the solution of potassium osmite and alkaline salts. This solution with the suspended powder is to be poured into a beaker and allowed to settle. The heavy black powder remaining in the iron pot is then to be perfectly dried over the fire, and fused a second time with potash and saltpetre as before. The fused mass is to be treated exactly as after the first fusion. The heavy portions remaining after this operation may be fused a third time with the oxidising mixture. When, however, the ore has been previously purified by fusion with sodium carbonate or when it was originally in the form of clean scales, the heavy portion remaining after two successive oxidations will be found to consist chiefly of scales of iron oxide.

The solutions containing potassium osmite and alkaline salts are to be carefully drawn off by a syphon from the black oxides which have settled to the bottom of the containing vessels. The oxides may then be washed with hot water containing a little alcohol, and introduced into a capacious retort. By this process, when carefully executed, no trace of osmic acid escapes—an advantage not to be despised, as the deleterious effects of this body upon the lungs have not been exaggerated, and too much care cannot be taken to avoid inhaling it.

The solution of alkaline salts contains only a portion of the osmium in the ore. The other portion exists in the mixture of oxide, and must be separated by distillation. For this purpose the retort should be provided with a safety-tube, passing through the tubulure, and with a receiver kept cold, and connected by a wide bent tube with a series of two or three two-necked bottles containing a strong solution of caustic potash with a little alcohol, and also kept cold. All the tubulures and connections must be made perfectly tight. Strong hydrochloric acid is then to be cautiously poured into the retort, through the safety-tube, in small portions at a time. The reaction which ensues is often violent; great heat is evolved, and a portion of the osmic acid distils over immediately, and condenses in the receiver in the form of colourless needles. When a large excess of acid has been added, the action has entirely ceased, and the retort has become cold, heat may be applied by means of a sand-bath. The osmic acid gradually distils over, and condenses in the receiver and in the two-necked bottles. Especial care must be taken that the neck of the retort is not too small at the extremity, as it may otherwise become completely stopped up with the condensed osmic acid. The same applies to the tubes connecting the receivers and two-necked bottles. The distillation should be continued for some time after osmic acid ceases to appear in the neck

of the retort; when this has once become hot, the acid condenses and passes into the receiver in the form of oily drops.

When the distillation is finished, the retort is to be allowed to cool, and then separated from the receiver, which is to be immediately closed with a cork. By gently heating the receiver in a water-bath, the contained osmic acid may be driven over into the two-necked bottles, where it condenses in the alkaline solution, and is reduced by the alcohol to potassium osmite. The solution thus obtained may be added to that obtained directly from the fused mass of ore, and on evaporation in a water-bath and cooling, will yield crystals of potassium osmite, the salt being but slightly soluble in strong saline solutions. The mother-liquor from the crystals contains only traces of osmium, and may be thrown away as worthless.

The dissolved portions drawn off from the retort have a very dark brown-red colour. The solution is to be evaporated to dryness, redissolved in hot water and again evaporated, after adding a little hydrochloric acid, and this process repeated till no smell of osmic acid can be perceived. A cold and saturated solution of potassium chloride is then to be added in large excess. This dissolves the iron and palladium chlorides which may be present, leaving platinum, iridium, rhodium, and ruthenium as double chlorides, insoluble in a strong solution of the alkaline chloride.

The undissolved mass is to be well washed with a saturated solution of potassium chloride, which is preferable to sal-ammoniac. In this manner nearly the whole of the iron and palladium may be removed, while any insoluble impurities contained in the ore remain with the mixed double chlorides.

For the separation of osmium from the other metals of the group, the best plan seems to be the one which is universally employed, namely, the volatilisation of the osmium in the form of osmic acid.

RUTHENIUM.

Preparation of Ruthenium from Osmide of Iridium (Osm-Iridium).

Osm-iridium almost always contains ruthenium, the amount of the latter metal increasing as that of the iridium decreases. The following process is the one recommended by Dr. Claus, the discoverer of ruthenium, for preparing this metal.

Osm-iridium is melted in the ordinary way with nitre and caustic potash, and moistened with water; then nearly neutralise with sulphuric acid, in order to precipitate the metallic acids in solution, always leaving the liquid with a slight alkaline reaction; add alcohol and boil. Throw the mixture on a filter, and carefully wash in order to free it as far as possible from potassium salts. The black metallic powder thus obtained still contains sufficient potassium in the state of

acid potassium iridiate to convert the greater portion of the iridium into double iridic chloride during the subsequent solution of the metallic powder. For this reason evaporate to a considerable extent the aqua regia solution separated from the powder until all the osmium is disengaged as osmic acid; then, if left to cool, most of the iridium is deposited in the state of potassium iridiochloride, and the liquid contains all the ruthenium in a much greater degree of concentration, although always associated with some iridium.

Afterwards filter and add powdered sal-ammoniac, which causes the deposition of yet more iridium as a black crystalline precipitate. The solution generally contains ruthenium so concentrated as to be separable from the iridium by precipitation. Now evaporate again and add more sal-ammoniac until the liquid begins to lose its colour, and most of the platinum metals are deposited as double salts. Then leave it for several days, collect the residue on a filter and wash it with water containing sal-ammoniac in solution, which completely eliminates iron and copper, and does not affect the ruthenium. In this way there is obtained a residue of iridium salts containing ruthenium, which, dissolved and boiled with the addition of a little ammonia, yields a precipitate of ruthenium sesquioxide.

Commenting on the above process, Dr. Gibbs says that this method of treating the fused mass to separate ruthenium and osmium is liable to two sources of inconvenience. In the first place, the quantity of water required to dissolve out the soluble portions is very large, and the subsequent treatment of such bulky solutions by distillation with acids is tedious, very large retorts being necessary. In the next place, it is impossible in this way to avoid exposure to the vapour of osmic acid, especially in transferring the solutions from one vessel to another. He therefore recommends the process which we have given at page 466.

Estimation of Ruthenium.

When it is necessary to estimate ruthenium precisely, the osmium must not be expelled previously by means of aqua regia, otherwise there would be some loss of ruthenium. For the estimation of ruthenium, a larger quantity of the alloy than is generally used is required—that is to say, at least 10 grammes, which must all be reserved for the search for ruthenium, disregarding all the other constituents. Melt the pulverised ore with potash and saltpetre, dissolve it in water, carefully neutralise it with an acid, and, adding some alcohol, heat it; then carefully wash the precipitate, which is a black metallic powder, in water, to eliminate the saltpetre and other potassium salts. Dissolve this powder in hydrochloric acid, heat it in a retort with potassium chlorate and hydrochloric acid, and collect the volatile products in condensers containing alcohol. By this means ruthenium and osmium are obtained together, but their separation can

be effected by alcohol, which instantly decomposes the ruthenic acid, though it takes some time to reduce the osmic acid ; or the two metals may be precipitated from their solution by sulphuretted hydrogen, and the sulphides thus obtained heated in a small platinum vessel, in an oxygen current, which disengages sulphur and osmium as acids, while the ruthenium remains as ruthenic oxide.

There is no appreciable loss in melting ruthenium with caustic potash and saltpetre. A piece of paper soaked with alcohol does not blacken if held even for a long time over the heated mixture, and no smell of ruthenic acid is observable, though during the solution of the mixture a feeble odour of it is always given off. If ruthenious sesquioxide, which is obtained by treating this solution with alcohol, is dissolved in hydrochloric acid, the solution takes place without forming a volatile ruthenic combination ; but there is some likelihood of loss if aqua regia is used as a solvent, for ruthenium is then placed under circumstances similar to those produced by the simultaneous action of potassium chlorate and hydrochloric acid.

Detection of Ruthenium in the Presence of Iridium, &c.

The reactions of ruthenium are remarkably affected by the presence of iridium ; and in proportion as this last-named metal is present in larger quantity, the indications afforded by most of the tests hitherto proposed grow less and less decided, and some lose all efficacy. Mr. C. Lea has discovered in sodium thiosulphate a very delicate test for ruthenium.

When a solution of sodium thiosulphate is mixed with ammonia, and a few drops of solution of ruthenium sesquichloride are added, and the whole boiled, a magnificent red-purple liquid is produced, which, unless the solutions are very dilute, is black by transmitted light. The coloration is permanent, and the liquid may be exposed to the air without alteration. This reaction is obtained with great ease and certainty, and, in the opinion of the discoverer, is far superior to any known test for ruthenium. In order to determine the limits of the sensibility of this reagent, experiments were made with ruthenium solutions of different strengths. The following results were obtained :—

With $\frac{1}{30000}$ of ruthenium sesquichloride, bright rose-purple.

With $\frac{1}{30000}$ and $\frac{1}{30000}$, fine rose colour.

With $\frac{1}{30000}$, paler, but still perfectly distinct.

With $\frac{1}{100000}$, the colour, though very pale, was still unmistakably present.

Where the solutions are so very dilute as these last, the boiling must be continued for some minutes.

When the presence of ruthenium in very small quantity, or in very dilute solution, is suspected, it is often advisable to boil the solution with a little hydrochloric acid, previous to the application of the thio-

sulphate test. The acidulated solution must be rendered alkaline by addition of ammonia before heating with thiosulphate.

This reagent is the best test that is capable of detecting ruthenium in the presence of any excess of iridium. No precautions are necessary, and the reaction is always obtained with the greatest facility. The iridium solution is to be rendered alkaline with ammonia, a crystal of sodium thiosulphate is dropped into it, and the whole is boiled for 2 or 3 minutes. If no indication of a red-purple tint appears (or, in case of small quantities of ruthenium, a rose colour), the iridium solution may be pronounced free from ruthenium.

Dr. Wolcott Gibbs has discovered another delicate test for ruthenium, which likewise can be employed in the presence of other platinum metals. When a solution of potassium nitrite is added in excess to ruthenium sesquichloride, either free, or in combination with potassium or ammonium chloride, a yellow or orange-yellow colour is produced, but no precipitate is formed. A precisely similar change occurs when the ruthenium is in the form of bichloride; but in this case the change of colour is produced more slowly, and usually requires heating or even boiling. The change of colour is due in both cases to the formation of an orange-yellow ruthenium and potassium double salt, which is very soluble in water and alcohol; its relations to alcohol in particular enable us to distinguish ruthenium from the other platinum metals more perfectly than has hitherto been possible. When a few drops of ammonium sulphide are added to a solution of this double salt a magnificent crimson colour is produced. This reaction furnishes a characteristic test of the greatest value, since it is not materially affected by the presence of the other metals of the same group.

The test may be most advantageously applied as follows:—The liquid supposed to contain ruthenium is first to be rendered alkaline by the addition of sodium or potassium carbonate. Potassium nitrite in solution is then to be added, the liquid boiled for an instant, allowed to become perfectly cold, and a drop or two of colourless ammonium sulphide added. On shaking, the colour appears, and rapidly deepens to the finest red. When the quantity of ruthenium present is very small, or when large quantities of the other platinum metals are also present, it is better, after adding the alkaline carbonate and nitrite, to evaporate the whole to perfect dryness on a water-bath, and treat the dry and powdered mass with a small quantity of absolute alcohol. The alcoholic solution is then to be filtered off, and tested directly with ammonium sulphide. In this way the smallest trace of ruthenium may be detected even in the presence of very large quantities of the other platinum metals.

Dr. Claus detects ruthenium qualitatively in the presence of iridium by making use of the following reactions:—A solution of pure iridium, containing no ruthenium, is instantly decolourised by the addition of excess of caustic potash or ammonia. It remains thus for a

long time perfectly transparent, and then, after several days, takes a beautiful blue colour. But if the iridium contains traces of ruthenium, the colour of the solution becomes fainter during the reaction, but does not disappear; it passes to a yellow-brown or reddish hue, and does not become decolourised for some time, at which point the solution becomes turbid, and a slight brown or yellow precipitate is formed. If the iridium contains more ruthenium, yet not sufficient to produce a visible precipitate, its presence is betrayed by the intense red-purple colour assumed by the liquid, especially if potash is used.

Separation of Ruthenium from Iridium.

The quantitative separation of ruthenium from iridium is much more difficult than the mere detection of ruthenium in the presence of iridium. Their separation cannot be effected by igniting them with a mixture of saltpetre and caustic potash. The following is an accurate means of separating the two metals, based upon Dr. Gibbs's discovery of the reaction of alkaline nitrites on ruthenium salts, described above:—

To the solution containing the two metals, sodium nitrite is to be added in excess, together with sufficient sodium carbonate to keep the liquid neutral or alkaline. The whole is to be boiled until the solution assumes a clear orange-yellow or orange colour. If a green tint should be perceptible, more sodium nitrite must be added, and the solution again boiled. Both ruthenium and iridium are converted into soluble double nitrites. A solution of sodium sulphide is then to be added, in small quantities at a time, until a little of the precipitated ruthenium sulphide is dissolved in the excess of alkaline sulphide. The first addition of the sulphide gives the characteristic crimson tint due to the presence of ruthenium, but this quickly disappears and gives place to a bright chocolate-coloured precipitate. The solution is then boiled for a few minutes, allowed to become perfectly cold, and then dilute hydrochloric acid added cautiously until the dissolved ruthenium sulphide is precipitated and the reaction is just perceptibly acid. The solution is then to be filtered through a double filter, and the ruthenium sulphide washed continuously and thoroughly with boiling water. The filtrate is perfectly free from ruthenium; it is to be evaporated with hydrochloric acid, and treated with sal-ammoniac in the manner already pointed out in speaking of the separation of iridium from platinum (page 469). The washed ruthenium sulphide is to be treated, together with the filter, with strong hydrochloric acid, and ammonium chloride added in sufficient quantity to form ammonium rutheniochloride. Nitric acid is to be added from time to time, in small quantities, until, with the aid of heat, the whole of the ruthenium sulphide is oxidised and dissolved. The liquid is then to be filtered, the filter well washed, and the filtrate and washings evaporated to dryness on a water-bath, when, after washing out the soluble salt with

strong solution of ammonium chloride, the ammonium rutheniochloride remains almost chemically pure. It is to be dissolved and converted into the compound of mercury and ruthendiamin chloride (see Separation of Ruthenium from Platinum). From this salt chemically pure ruthenium may be obtained by ignition, which is best effected in an atmosphere of hydrogen, as the reduced metal is easily oxidised in the air.

It may happen that the precipitated ruthenium sulphide contains traces of iridium. This can only arise from imperfect washing or want of proper care in precipitating with sodium sulphide. In this case, the washings from the ammonium rutheniochloride are yellow, and contain iridium sulphate. The quantity of iridium in such cases is too small to be worth the trouble of separate treatment.

When a solution contains iridium and ruthenium in the form of bichlorides, the ruthenium may be easily and completely separated by boiling the solution with potassium nitrite in excess, adding, at the same time, enough potassium carbonate to give an alkaline reaction, evaporating to dryness, and dissolving out the double ruthenium and potassium nitrite by means of absolute alcohol. The undissolved mass in this case contains two double iridium and potassium nitrites. By adding a strong solution of ammonium chloride, evaporating to dryness, igniting the dry mass in a porcelain crucible, and dissolving out the soluble salts, metallic iridium remains in a state of purity. This method may be used for quantitative separation of iridium from ruthenium; but when the object is simply to prepare both metals in a state of chemical purity, the separation by means of sodium sulphide is preferable.

Separation of Ruthenium from Rhodium.

The separation of rhodium from ruthenium is best effected by means of potassium nitrite. The mixed solution of the two metals is to be boiled for a short time with an excess of the nitrite, together with a little potassium carbonate to keep the solution neutral or slightly alkaline. The yellow or orange-yellow solution is then to be evaporated to dryness upon a water-bath, the dry mass rubbed to fine powder and then treated in a flask with absolute alcohol in the manner pointed out for the separation of ruthenium from platinum. After filtration and washing with absolute alcohol, the rhodium remains undissolved in the form of a mixture of the two double rhodium and potassium nitrites. These may be ignited with a large excess of sal-ammoniac, so as to yield, after washing, metallic rhodium; or the nitrites may be dissolved in hot hydrochloric acid, ammonia added, and the rhodium precipitated as sulphide, which is then treated in the manner already pointed out (page 464), so as to convert the rhodium into the double rhodium and ammonium chloride. To remove the last traces of ruthenium the rhodium salt may be a second time treated

with potassium nitrite, as above, and again washed with alcohol. The presence of the least trace of ruthenium is easily detected by adding a drop of colourless ammonium sulphide to the alcoholic solution. The method of obtaining pure ruthenium from the double ruthenium and potassium nitrite has already been given.

Separation of Ruthenium from Platinum.

The approximate separation of ruthenium from platinum may be effected by precipitating the two metals with potassium chloride and washing out the potassium rutheniochloride with cold water, in which it is readily soluble. The mixed solutions should be evaporated to dryness with an excess of the alkaline chloride, and the dry mass rubbed to a fine powder in a mortar, after which almost the whole of the ruthenium may be washed out with water, or with a cold and moderately strong solution of potassium chloride. The undissolved platinum salt may then be purified by crystallisation, but it usually contains traces of ruthenium. The rose-red solution of the ruthenium salt contains a small quantity of platinum, from which it cannot be wholly freed by the difference in solubility of the two salts. Ammonium chloride may be employed in this process in place of potassium chloride.

To obtain a complete separation, Dr. W. Gibbs's process may be followed with advantage:—The potassium rutheniochloride, separated as far as possible from the platinum salt, is to be heated with a solution of potassium nitrite in quantity sufficient to convert the whole of the ruthenium into the soluble yellow double ruthenium and potassium nitrite, potassium carbonate being added in small quantities so as to keep the solution neutral or alkaline. The yellow or orange solution is to be evaporated to dryness in a water-bath, the dry mass reduced to powder and boiled with absolute alcohol until the ruthenium salt is completely dissolved. This is best effected in a flask furnished with a condensing-tube bent upwards, so that the alcohol vapours may be condensed and flow back into the flask. The boiling need not be continued for a very long time, as the ruthenium salt is readily soluble in alcohol. The solution is then to be filtered off from the undissolved salts, and these are to be washed with absolute alcohol until the washings are colourless, or until they no longer give the characteristic ruthenium reaction with ammonium sulphide. The filtrate and washings may then be distilled, to separate and save the alcohol, water being added in small quantity. The residue in the retort or flask is then to be evaporated with hydrochloric acid, which readily decomposes the double nitrite, and yields a fine deep rose-red solution of the potassium rutheniochloride, containing at most only a trace of platinum. The mass of salts undissolved by the alcohol contains nearly all the platinum in the form of potassium platinochloride, which is easily separated. The solution of the potassium rutheniochloride is now so pure that it gives the reactions of a chemically pure salt.

To obtain the ruthenium in a state of absolute purity, the solution is to be evaporated to dryness with a saturated solution of sal-ammoniac in excess, redissolved, again evaporated, and the dry mass washed with a little cold water to remove the alkaline chlorides. The potassium rutheniochloride is in this manner, for the most part at least, converted into the corresponding ammonium salt. This salt is then to be dissolved in hot water, a solution of ammonia added, and the liquid boiled until it assumes a clear yellow or orange-yellow colour, after which it is to be evaporated to dryness on a water-bath. In this manner the ruthenium is converted into ruthendiamin chloride, discovered by Claus. The yellow mass is to be dissolved in boiling water, and a solution of mercury chloride added. A beautiful yellow crystalline double salt is precipitated, and the mother-liquor, when cold, contains only traces of ruthenium and platinum. The double mercury and ruthendiamin chloride is almost insoluble in cold water, but is soluble in boiling water, and is easily rendered absolutely pure by recrystallisation. On ignition, this salt yields chemically pure metallic ruthenium as a silver-white porous mass.

When, in a mixture of solutions of ruthenium and platinum, the ruthenium is present either partly or wholly as sesquichloride, the liquid is to be boiled with potassium nitrite and carbonate as above, evaporated to dryness, boiled with excess of hydrochloric acid to convert the double ruthenium and potassium nitrite into potassium rutheniochloride, and the resulting solution treated by the process already described.

CHAPTER XI.

SULPHUR, PHOSPHORUS, NITROGEN.

SULPHUR.

Estimation of Sulphur in Pyrites.

A. Estimation of Sulphur in the Dry Way.—Fuse the weighed ore with a weighed quantity of anhydrous sodium carbonate, twice as much potassium chlorate as ore, and from 12 to 20 times as much sodium chloride (added to moderate the action); carbonic acid is expelled, potassium chloride formed, and all the sulphur converted into sodium sulphate; by dissolving the residue in water and estimating alkali-metrically the unaltered sodium carbonate by a standard acid solution, the portion converted into sulphate, and hence the sulphur in the ore, is known. Besides the difficulty of preventing loss by deflagration, this method is open to the small errors caused by the reckoning all arsenic present to be sulphur: this, however, is usually of no moment for commercial purposes; any calcium carbonate in the ore may, if required, be previously dissolved out by dilute hydrochloric acid.

In performing fusions of sulphur compounds with nitre or potassium chlorate, the operator must bear in mind a source of error, first pointed out by Dr. David S. Price, in consequence of sulphur compounds being contained in the coal-gas which frequently serves as fuel in these experiments. By exposing a small quantity of melted nitre, on the *outside* of a platinum capsule, to the flame of a Bunsen gas-burner for three-quarters of an hour, Dr. Price succeeded in detecting the presence of sulphuric acid to an amount equivalent to 12 milligrammes of sulphur. This sulphuric acid had been formed by the oxidation of the sulphur in the coal-gas, and, when dissolved in water, gave an immediate precipitate with barium chloride. By making a similar experiment with the use of a spirit-lamp as the source of heat, no trace of potassium sulphate was formed; nor was any appreciable amount of sulphuric acid generated in another trial made by fusing a small quantity of nitre *inside* a platinum capsule heated over gas; but whenever the fused salt crept over the edges of the capsule, some of the sulphate was sure to be formed. This observation may become a matter of importance when the amount of sulphur in pig-iron is estimated by fusion with pure nitre, for the author has remarked that samples containing

much manganese are especially liable to impart to the fused salt a tendency to creep up and escape over the sides of the crucible.

The following process obviates some of the difficulties just mentioned:—One gramme pyrites is mixed in a large covered crucible with 8 grammes of a mixture of equal parts—potassium chlorate, sodium carbonate, and sodium chloride. The crucible is heated at first gently so as to dry the contents, which are afterwards melted at a high temperature. The mass when cold is treated with boiling water, and the solution, together with the deposit, is introduced into a measuring flask of 200 c.c. filled up, filtered, and the sulphuric acid is estimated in aliquot parts, say 50 c.c. The insoluble residue does not retain any sulphuric acid. In this manner the use of nitric acid is evaded. The decomposition of the potassium chlorate is complete.

The following is a useful modification of the potassium chlorate method:—Half a gramme of finely-ground pyrites (sifting is not absolutely necessary) is mixed in a large platinum capsule, with the well-known mixture of 6 parts sodium carbonate and 1 part potassium chlorate. The mixing is effected with a platinum spatula, and is then made more complete by gentle rubbing with an agate pestle fixed to a wooden handle. The whole is then fused over the blow-lamp. The aqueous solution of the melt is first poured into a beaker to avoid spirting, and then into another tall beaker containing an excess of hydrochloric acid. The filtered solution is heated and precipitated with hot barium chloride, heated gently upon the sand-bath for a time, until the liquid standing above the precipitate has become clear, and is filtered at once. The burnt ores in sulphuric acid works have been for a long time assayed for sulphur by this process. From 20 to 25 grammes of chlorate mixture are required for 2 grammes of burnt ore.

If sulphur is fused with a sufficient excess of alkali it is converted entirely into sulphite, and not into a mixture of thiosulphate and sulphide, and if still more alkali is present, the result is a mixture of sulphite and sulphate. To oxidise the sulphite to sulphate, bromine is used. This analytical principle may be successfully applied to organic sulphur compounds, to free sulphur, and metallic sulphides. The fusion of sulphur or a metallic sulphide with potash yields a sulphite without any loss, which is then oxidised by means of bromine and hydrochloric acid, forming sulphuric acid, and then estimated in the ordinary manner. Where metallic oxides are separated after the fusion in an insoluble state, they are removed by filtration before the bromine and hydrochloric acid are added. Arsenic, antimony, zinc, &c. sulphides all yield, after melting, a fusible mass, whilst in the case of iron and copper sulphides these metals are left behind in the state of oxides. Even in pyritic silicates the sulphur can be accurately estimated in this manner. Care must be taken that not less than 25 grammes pure caustic potash are taken to every 0.1 gramme of sulphur supposed to be present. The operation is performed in a silver crucible, and the

fusion is continued till all the mixture becomes tranquil—say from 15 to 20 minutes—or till the vapours of alkali begin to condense along the upper part of the crucible, which after use shows a clean surface if sufficient alkali has been used. When cold the mass is dissolved in cold water, freed from oxides, &c. by filtration, mixed with from 75 to 100 c.c. bromine-water, and hydrochloric acid added till a distinctly acid reaction is obtained. Heat is then applied till the liquid is colourless.

The pyrites may also be burnt in a current of oxygen, and the products of combustion titrated. The operation is carried on in a tube of green glass, placed in a furnace for organic analysis. One end of the tube is sealed, and to the other is fitted a stopper with two holes. One of these serves for the escape of the gaseous products of combustion, which are received in a Liebig's bulb apparatus containing standard caustic soda. Through the other hole passes a long narrow tube, which conveys oxygen, free from water and carbonic acid, to a small platinum boat placed near the closed end of the combustion-tube, and containing $\frac{1}{2}$ gramme of the pyrites spread out in a thin layer. A plug of asbestos is placed about the middle of the tube, to avoid projections. Heat is first applied towards the open end of the tube, and as it approaches redness it is gradually extended towards the closed end. The current of oxygen is regulated so as to be always in excess. The disappearance of the white vapours formed in the bulb tube during the operation is a sign that the sulphurous acid is expelled from the combustion-tube. The open end of the tube and the stopper are then washed, and the washings are added to the liquid in the bulb tube, the sulphurous acid in which is then estimated in the usual manner. If the pyrites contain carbonates, standard solutions cannot be used. It is then necessary to oxidise the sulphurous acid and estimate the sulphuric acid formed.

The following process, due to Mr. P. Holland, will be useful in laboratories which do not possess large platinum crucibles. A test-tube or piece of sealed combustion-tube, about 6 inches long and $\frac{1}{2}$ inch internal width, is fitted with a cork and delivery-tube, the latter bent at a right angle and long enough to reach to the bottom of the flask in which it is intended to make the titration. The fusion mixture consists of equal parts of nitre and ignited acid sodium carbonate, both free from sulphur, dry, and in fine powder. Nine to ten grammes are taken in an operation, together with one of pyrites, the latter must be in exceedingly fine powder; the two are mixed in a warm porcelain dish, or agate mortar, and transferred to the tube without loss. The delivery-tube is then inserted with its extremity dipping into the flask. A channel is made on the surface of the mixture, and the tube, suitably supported, is heated in small portions at a time with a Bunsen gas-flame, commencing as usual with the anterior portion. When the operation is progressing favourably, the deflagration proceeds for a few seconds after removing the flame.

There is no danger to be apprehended, and with proper care the tube does not crack or blow out. When the tube has been heated throughout, and the deflagration has ceased, it is then more strongly heated with a Herapath or powerful gas-flame. It is a good plan at this stage to slip a coil of wire gauze over the tube, which helps to accumulate the heat. It is not, however, necessary that the contents should be fused a second time. The sulphur ores examined yielded their sulphur readily.

The gaseous products of the combustion which mechanically carry over with them small quantities of sulphates or sulphuric acid, being heavier than air, collect in the flask, and are washed by shaking with a little water, closing the flask with the palm of the hand. The delivery-tube is also washed. That containing the fused mass is carefully broken and put in the flask, together with sufficient hydrochloric acid to dissolve nearly the whole of the oxide; then ammonia is added until a precipitate of oxide reappears, and, lastly, as much free hydrochloric acid and water as are necessary to bring the fluid to the conditions which were obtained when the barium solution was standardised. 2 c.c. of free acid may be used when the total volume of solution is 200 c.c.

B. Estimation of Sulphur in the Wet Way.—Dr. C. R. A. Wright recommends the following process as being the one best adapted for commercial purposes:—A known weight of the ore reduced to fine powder is oxidised (best in a small flask with a funnel placed in the mouth to avoid loss by spiriting, and heated on a sand-bath) either by strong nitric acid or aqua regia perfectly free from sulphuric acid; after the oxidation is complete, the liquid is evaporated down as far as possible to expel the majority of the remaining nitric or hydrochloric acid; the residue is boiled with a little water, and almost but not quite neutralised by ammonia; a solution of barium chloride of known strength is then added until no further precipitate is produced, the exact point being found by filtering off a little of the liquid after each addition of barium chloride and adding to it a few more drops of the standard solution, care being always taken, in case of a further precipitate being thus produced, to add this filtrate to the original solution, and mix well before filtering a second time. In case of overstepping the mark, it is convenient to have at hand a solution of sodium sulphate of strength precisely equal to that of the barium chloride; this solution may then be cautiously added, with repeated filtration and examination of the filtrate with the sulphate solution, until the point is just reached, when addition of sulphate solution produces no further precipitate; by subtracting the volume of sulphate solution thus used from the total volume of barium solution added, the exact quantity of this latter consumed is known. If 1 gramme of sulphur ore be taken, and 82.5 grammes of pure anhydrous barium chloride be dissolved to a litre of fluid, each cubic

centimetre of barium solution used will represent $\frac{1}{2}$ per cent. of sulphur in the ore examined; 22.19 grammes of anhydrous sodium sulphate being dissolved to a litre for the second solution. In case of lead being contained in the ore, an error is introduced from the formation of insoluble lead sulphate; as lead, however, rarely occurs in any perceptible quantity, this error is negligible, the process only giving approximate results.

Where greater accuracy is required, it is advisable to precipitate the sulphuric acid formed from the original liquid (filtered from insoluble residue) by barium chloride or nitrate, and to weigh the barium sulphate produced. Instead of oxidising by acids, the powdered ore may be suspended in caustic potash (free from sulphate), and oxidised by passing washed chlorine into the liquid; lead, being converted into dioxide, is thus rendered non-injurious; the alkaline liquid obtained is acidified and precipitated by barium chloride as before. In the volumetric estimation usually pursued, a curious circumstance is occasionally observable when much free acid exists in the solution, viz. that a point may be reached when the filtered liquid is clear, and remains so even on standing for a short time, but yields a cloud, or even a precipitate, on the addition either of barium solution or sulphate solution; this source of error is mostly avoidable by nearly neutralising the free acid with ammonia.

Instead of chlorine, hypochlorous acid may be used to transform the sulphur of pyrites into sulphuric acid, which is then estimated by barium. Finely pulverise the mineral and suspend it in water, through which a current of gaseous hypochlorous acid, or, better still, hypochloric acid, is passed; this entirely dissolves the pyrites. Hypochloric acid is prepared by heating a milk of calcium carbonate through which a current of chlorine is passed to saturation. Hypochloric acid is also obtained by heating in a water-bath a tube, supplied with a cork and delivery-tube, and containing a mixture of 9 equivalents of oxalic acid and 1 equivalent of potassium chlorate.

1.37 g
Mr. A. H. Pearson has given the following very accurate method of estimating sulphur in pyrites:—Weigh out 1 gramme or less of the powdered ore, place the powder in a porcelain dish, together with a small quantity of potassium chlorate, pour upon it some 50 c.c. of pure nitric acid of 39° B., and cover the mixture with an inverted glass funnel with bent stem. Set the dish upon a water-bath, and heat the water to boiling. From time to time throw crystals of potassium chlorate into the hot acid. By adding rather large crystals of the chlorate at frequent intervals, it is easy to oxidise the whole of the sulphide in half an hour; but, since the solution obtained in that case is highly charged with saline matter, it will usually be found more advantageous to use less of the potassium chlorate and to allow a somewhat longer time for the process of oxidation.

When all the sulphur has been oxidised, rinse the funnel with

water and remove it from the dish. Evaporate the liquid to a small bulk, then add to it a little concentrated hydrochloric acid, and again evaporate to absolute dryness, in order to render silicic acid insoluble. Moisten the residue with concentrated hydrochloric acid, mix it with water, and filter to separate silicic acid and gangue.

To the filtrate from the silicic acid add a quantity of solid tartaric acid, about as large as that of the pyrites originally taken; heat the liquid almost to boiling, and add to it an excess of barium chloride, to precipitate the sulphuric acid. After the barium sulphate has been allowed to subside, wash it thoroughly by decantation, first with hot water and afterwards with a dilute solution of ammonium acetate (the latter may be prepared at the moment of using by mixing ammonia-water and acetic acid). The purpose of the ammonium acetate is to dissolve any barium nitrate which may adhere to the sulphate; that of the tartaric acid is to prevent the precipitation of iron compounds together with the barium sulphate. In an experiment where 0.7 gramme of pyrites was oxidised with potassium chlorate and nitric acid, and the filtrate from silica was acidulated with hydrochloric acid without the addition of tartaric acid, there was thrown down, on the addition of barium chloride, a bright yellow precipitate, which became darker coloured when the solution was boiled. It was not only found to be impossible to wash out the iron with which this precipitate was contaminated, but the consistency of the precipitate was such that it was a difficult matter even to wash away the saline liquor in which it was formed.

In another experiment, the attempt was made to remove the iron in the filtrate from silica, before adding the barium salt to throw down the sulphuric acid; but in that case a considerable portion of the sulphuric acid was dragged down as potassium sulphate by the iron precipitate, and so lost. The precipitation of the iron was effected, in this experiment, by adding an excess of ammonia-water to the acidulated filtrate from silica, and washing the precipitate for a long time by decantation with boiling water. To prove that the iron precipitate really retained sulphuric acid, a quantity of the precipitate was dried, ignited, and powdered, and the powder boiled with water. The clear liquid thus obtained was acidulated with hydrochloric acid, and tested with barium chloride. An abundant precipitate of barium sulphate was at once thrown down.

Errors of 1.5 to 4 per cent. are often made if the nitric acid employed in oxidising the sulphur is not driven off by the subsequent application of an excess of hydrochloric acid. If this precaution is omitted, the barium sulphate thrown down in presence of free nitric acid is somewhat soluble, and if abundantly washed, the result is too low. If, on the other hand, the washing is but slight, a quantity of barium nitrate may remain mechanically mixed with the sulphate, and the result is too high.

R. Fresenius shows that the precipitation of barium sulphate, in boiling solutions, does not take place instantaneously. Appreciable quantities remain at first in solution. If the solution contains ferric chloride, this has, on the one hand, a solvent action upon the barium sulphate, which, on the other hand, always appears red after ignition, and the ferric oxide producing this colour cannot be removed by treatment with hot hydrochloric acid. These two sources of error act in opposite directions, but the solvent action of the hydrochloric acid and the ferric chloride preponderates. In an examination of Lunge's process (precipitation of the boiling liquid containing ferric chloride, and some hydrochloric acid, with boiling barium chloride and immediate filtration), Fresenius has obtained deficiencies of 1 to 1.7 per cent. in a pyrites containing 48.8 per cent. of sulphur, as ascertained by his own method.

On the other hand, G. Lunge maintains that his process, though yielding results less absolutely accurate than those obtained by the method of Fresenius, is yet preferable for use in chemical works where time is the first object. He thinks that the larger proportion of sulphur obtained by the process of Fresenius is partly due to the fact, that both galena and heavy spar—bodies frequently found in pyrites—are attacked by the dry process.

Lead sulphide, and lead and copper ores in which it occurs, cannot be dissolved in nitric acid without the deposition of lead sulphate, which contains, also, lead antimoniate, if antimony is present. The estimation of the metals in such cases is easy if the compound is dissolved by boiling in hydrochloric acid. Even ores rich in copper dissolve completely. The hot solution is finally allowed to flow into dilute sulphuric acid, to prevent the deposition of lead chloride.

P. Waage calls attention to the drawbacks of nitric acid, chlorine, and potassium chlorate with hydrochloric acid, and recommends bromine, which he has used with success for two and a half years for sulphur, magnetic pyrites, copper pyrites, mispickel, nickel mattes, and precipitated sulphides, both for the estimation of sulphuric acid and the metals.

Sulphur, shaken with bromine and water, is easily converted into hydrobromic and sulphuric acids, if for every atom of sulphur 8 of bromine are present, or 15 by weight of bromine to 1 of sulphur. If sulphur has to be estimated in this way, it is best to add all the bromine at once, so that no bromine sulphide can be formed.

In the treatment of pyrites no necessity will exist for pulverising them very finely, as they are oxidised by bromine quite easily even in larger pieces, but it is best to add water first, and then bromine with constant stirring, that the action may not become too violent.

Bromine-water is the most convenient material for the destruction of hydrosulphuric acid. A few drops of it added to a filtrate from a metallic sulphide will immediately produce a separation of sulphur,

which will as quickly be dissolved by a further addition of a few drops of bromine-water.

In dissolving precipitated metallic sulphides proceed in the following manner:—Perforate the filter-paper and wash as much of the precipitate as possible into a beaker. Then pour some of the bromine water into the funnel, and cover the latter with a watch-glass, when after a few minutes the rest of the sulphide may be washed into the same beaker, and a further addition of bromine-water readily oxidises the rest of the sulphide. We thus get rid altogether of the trouble of burning the filter-paper.

Reichardt, however, states that iron pyrites requires to be very finely pulverised, and a prolonged action is required. Copper pyrites is dissolved very rapidly if an excess of bromine is used, which is easily expelled by a gentle heat. The sample is placed in a small flask, covered with a little water, and the bromine is added. A gentle heat is sometimes necessary towards the end.

In a direct volumetric estimation of the sulphuric acid resulting from the oxidation of pyrites by the wet method, Mr. Philip Holland finds that it is desirable to titrate in presence of but little free hydrochloric acid in the entire absence of nitric acid, and to standardise the barium chloride by iron sulphate as nearly as possible under the conditions which will prevail in a pyrites assay so far as the amount of free acid and the volume of liquid are concerned.

Messrs. Glendenning & Edgar call attention to the inaccuracy introduced in the analysis of pyrites by the use of Wedgwood and porcelain mortars. The percentage of silica is in some cases doubled, and the sulphur necessarily diminished. They recommend to break up the sample in a steel mortar and pulverise in an agate mortar.

Estimation of Sulphur in Iron, Steel, and Iron Ores.

According to C. H. Piesse, a simple and ready method of estimating the sulphur in pig-irons and steels, and one requiring but little attention, is as follows:—Place in a beaker of about 900 c.c. capacity about 8·5 to 4 grammes of the sample in drillings (weighed to within 0·01 gramme will be sufficiently accurate), and pour upon them 35 to 40 c.c. of aqua regia, maintaining the proportion of 10 c.c. of the mixed acids for every 1 gramme of the metal, keeping the beaker covered as well as possible with a watch-glass. After the first violence of the action has subsided, boil the liquid for a few moments until the whole of the iron is dissolved, then transfer the solution with as little washing as possible to a porcelain basin, and evaporate nearly to dryness on a water-bath. Treat the residue with some concentrated hydrochloric acid, add about an equal bulk of water, and then filter. To the filtrate add a considerable excess of barium chloride solution, allow to stand for about 12 hours; filter, and weigh the precipitated barium sulphate with the usual precautions.

M. Koppmayer introduces 10 grammes of iron, finely powdered and sifted, into a bottle holding from $\frac{1}{2}$ to $\frac{3}{4}$ litre. The stopper has three holes. Through one of these passes a funnel with a ground-glass tap, its neck reaching to the bottom of the bottle. Through the second passes the tube at right angles, fitted with a tap, and reaching also to the bottom of the bottle. Through the third hole passes the delivery-tube, connecting the bottle to the condensing apparatus. This latter consists of a series of bulbs arranged like a staircase, so as to permit the gas to come into the greatest possible contact with the standard solution of iodine in potassium iodide with which the condenser is filled. This solution ought not to be exposed to light. When the apparatus is arranged as above, the air is first driven out of the bottle by means of a current of hydrogen gas introduced by the tube bent at right angles. When it is considered that the air is entirely expelled the tap of this tube is closed. The funnel is now filled with hydrochloric acid, its tap is opened, and by means of the application of heat the acid is allowed to run down upon the iron without allowing any air to enter. Hydrogen and sulphuretted hydrogen are formed, which pass into the condenser. Acid is thus added until all the disengagement of gas ceases. The bottle is then heated until its contents boil, a little water having been first added by means of the funnel. After these operations hydrogen is again allowed to enter so as to sweep out all remaining gases. The iodised solution is then poured in, care being taken to rinse the bulb tube thoroughly, and titrated with sodium thiosulphate, so as to find the remaining proportion of free iodine. The difference between the original amount of iodine present in the solution and the amount thus found shows the proportion of iodine which has been converted into hydriodic acid, and which is proportional to the sulphur contained in the sample under examination.

The common method of estimating sulphur in iron and steel consists in acting on the metal with sulphuric or hydrochloric acid, and precipitating some metallic sulphide by the evolved sulphuretted hydrogen. It would be a desideratum, in point of time, if this sulphide could be directly weighed.

Mr. T. J. Morrell passes the evolved gases through an ammoniacal solution of cadmium oxide (or a solution of sulphate to which an excess of ammonia has been added); a precipitate of cadmium sulphide is obtained, which can be at once collected upon a small filter, dried at 212° F., and weighed.

The phosphuretted hydrogen, evolved in a solution of the metal together with the sulphuretted hydrogen, causes no precipitation in the solution.

The presence of ammoniacal salts would also prevent any precipitation of cadmium carbonate by the traces of carbonic acid in the air, drawn through the apparatus by the aspirator after the metal is dissolved. However, the aspirated air could easily be passed through potash solution, to remove its carbonic acid.

To prevent the precipitation of cadmium oxide on the filter, the precipitate should be washed with distilled water containing diminishing quantities of ammonia.

If in very accurate analyses it is necessary to estimate the minute quantity of sulphur left in the solution and residue of the metal, this can be done as usual and added to that found as above.

Estimation of Sodium Sulphate.

Insoluble Matter.—Weigh 50 grammes of the sample, dissolve in 600 to 700 c.c. of distilled water, and filter into a flask marked at 1 litre. The insoluble matter remaining on the filter is washed into the flask, dried, and weighed after incineration. We do not in this manner obtain the full amount of the insoluble matters, since some of them are combustible, and are lost during ignition.

Free Acid.—The filtrate is made up to 1 litre, and well stirred so as to be homogeneous. By the aid of a pipette 800 c.c. are taken, placed in a beaker, and titrated with standard alkali in the usual manner.

Alumina and Iron Oxide.—200 c.c. of the filtrate are taken, and mixed with bromine-water to peroxidise the iron. Precipitate with ammonia, and weigh the mixed deposit of alumina and ferric oxide in the usual manner.

Calcium Sulphate.—To the filtrate from the alumina and iron oxide ammonium oxalate is added. The precipitate is collected on a filter, washed, ignited, treated with a few drops of sulphuric acid, diluted with an equal volume of water, ignited again, and weighed as sulphate.

Magnesium Sulphate.—To the liquid freed from lime, sodium ammoniaco-phosphate is added. The precipitate formed is converted by ignition into magnesium pyrophosphate, one part of which represents 1.08 of sulphate. Sodium chloride is estimated by titration in the well-known manner with silver nitrate, using potassium chromate as indicator. Water cannot be estimated directly, for before the water is expelled the sodium bisulphite reacts upon the sodium chloride. The sample is, therefore, heated to fusion, and the known amount of free acid deducted from the loss. A correction is still required on account of the loss of hydrochloric acid. For every 117 parts of chloride decomposed by fusion we must add to the loss 25 parts. To find the quantity of chloride thus decomposed, we dissolve the sample after fusion and re-estimate the chlorine.

Estimation of Sulphur in Vermilion.

A mixture of nitric acid and potassium chlorate is the best means of oxidising the sulphur in this mineral to sulphuric acid, as no trace of free sulphur is ever seen in the liquid, whilst when hydrochloric acid is used to decompose the chlorate, globules of sulphur float about and

entirely resist solution. About 0.5 or 0.6 of a gramme of the vermilion is placed in a small glass flask, set in an inclined position upon a wire-gauze support above a lamp. A quantity of nitric acid of 39° Beaumé is poured into the flask, a small quantity of potassium chlorate then added, and the mixture heated. From time to time crystals of potassium chlorate are thrown into the flask, the contents of which are maintained near the boiling-point until all the sulphur has dissolved. It sometimes happens, when the proportion of nitric acid is small, that a considerable quantity of saline matter crystallises in the flask; enough water to redissolve this precipitate may, however, be added to the mixture, without impairing to any material extent the oxidising power of the chlorate subsequently added.

The acid liquor resulting from the action of nitric acid and potassium chlorate upon the vermilion is evaporated to dryness on a water-bath, and the residue treated with strong hydrochloric acid, in order to destroy most of the nitric acid before proceeding to precipitate the sulphuric acid with barium chloride. Before adding the hydrochloric acid to the residue, the latter must be allowed to become perfectly cold, lest the mixture froth violently and portions of it be thrown out of the flask. After the acid has once been added, however, the mixture may be heated gently without risk of loss. The solution must at last be largely diluted with water before adding the barium chloride.

Estimation of Sulphur in Mineral Waters.

Mr. F. Maxwell Lyte has devised an ingenious method of estimating free sulphuretted hydrogen in a mineral water when accompanied by iron protosulphate, the presence of which interferes with the usual tests. Some lead sulphate is prepared by precipitation from boiling solutions, and is well washed with boiling distilled water, and, while still fresh and moist, successive portions are added to the mineral water till the brownish-black colour of the precipitate first formed turns to a decided grey, showing that the sulphuretted hydrogen has all been removed from the solution, and that some undecomposed lead salt remains in excess. The supernatant liquid is decanted from the precipitate, which rapidly settles down, and the latter is rapidly washed on a filter with boiling distilled water, and subsequently with hot solution of ammonium acetate to dissolve out the excess of lead sulphate, till the washings are no longer coloured by the addition of an alkaline sulphide. The filter is now carefully incinerated, and the lead sulphide oxidised by an addition of a little nitric acid, and evaporated with a little sulphuric acid until heavy fumes of the latter begin to be evolved. Subsequent dilution with water gives a precipitate of lead sulphate, which is separated by decantation and weighed; from this may be calculated the amount of sulphuretted hydrogen which has been present in the water.

For the estimation of hydrosulphuric acid in mineral waters,

Mr. W. J. Land gives the following directions :—In an apartment free from direct sunlight, preferably a room lighted by non-actinic rays, prepare a moist precipitate of *pure silver carbonate*, by dissolving 8·5 grammes of pure silver nitrate in one-fourth of a litre of distilled water ; also 2·7 grammes of chemically pure dry sodium carbonate in an equal volume of distilled water previously heated to about 180° F. Mix the solutions gradually, simultaneously stirring them with a glass rod. Allow the precipitate to subside, decant the supernatant liquid with a pipette or small syphon, wash with hot distilled water, decanting and washing successively five or six times to obtain a comparatively clean precipitate of silver carbonate, in which substance we have a most excellent reagent for removing every trace of hydrosulphuric acid, small quantities of alkaline sulphides and haloids, from their solution in water. Add to a definite quantity of the water to be operated upon (say 1 litre if strongly impregnated, and 10 litres if weakly impregnated with gas) the still moist precipitate of silver carbonate, until the precipitate, at first black in colour, becomes brown or greyish-brown, thus indicating an excess (as desired) of the silver salt. Shake or stir well, warm gently, and allow the precipitate to subside perfectly. Decant the greater part of the liquid, transfer the remainder of the liquid with every trace of the precipitate to a small beaker, and digest the latter with pure dilute nitric acid (1 of acid to about 4 of water), thus removing the excess of silver carbonate. Decant and wash well with distilled water. Transfer to a weighed filter, wash with a moderately dilute solution of ammonia (to remove silver haloids), testing the ammoniacal filtrate occasionally with ammonium sulphide, or other suitable reagent, to discover the presence or absence of the silver haloids in the washings ; when all traces of these have disappeared, wash well with distilled water, lastly, with pure 95 per cent. alcohol ; dry on a water-bath. Remove the dried silver sulphide from the filter, ignite the latter in a small porcelain crucible with a grain or two of sulphur, heating to incipient redness (to expel excess of sulphur), add the ignited product to the larger quantity of the precipitate, transfer to a desiccator, afterwards weigh. 124 parts of the sulphide correspond to 17 of hydrosulphuric acid sought.

Detection of Sulphur by Means of Sodium or Magnesium.

Dr. Schönner recommends the use of either of these two metals for ascertaining the presence of sulphur in the oxidised or non-oxidised state in compounds. The substance to be tested (for instance, calcium or barium sulphate) is thoroughly mixed, previously reduced to powder, and next heated to redness with the metal in a test-tube made of thin hard glass. After the reaction is over, the contents of the tube are, when quite cold, treated with distilled water and tested with sodium nitro-prusside. Care should be taken that only small quantities of substance are operated upon in this manner, especially as substances

like realgar, orpiment, and others containing sulphur and arsenic at the same time detonate violently when ignited with sodium.

As regards liquids containing sulphur, the author states that a drop of sulphuric acid, when brought into contact with sodium, yields, among the products of the reaction, sodium sulphide; with magnesium, this reaction does not take place unless heat be applied. Carbon disulphide and essential oil of mustard may be readily proved to contain sulphur by application of the same test. For detecting sulphur in organic substances, especially of animal origin, the same process is available. Hair and feathers, dry skin and nails, may be at once submitted to ignition with the metal. White of egg, emulsin, saliva, or muscle should first be calcined on a piece of platinum, and the animal charcoal so obtained be ignited along with sodium or magnesium. In most cases of this kind sodium nitro-prusside will be required to make the presence of sulphur distinctly evident.

Reagent for Sulphur.

According to Dr. Schlossberger, a solution of ammonium molybdate in hydrochloric acid, diluted with water, possesses the property of becoming coloured blue if traces of sulphur are present. By this means the presence of sulphur even in a single hair is easily recognisable after it is rendered soluble by the method just given.

Mr. Brunner mixes the substance under examination with strong potash lye, and adds a few drops of nitro-benzol and alcohol, and allows the mixture to stand at the common temperature. After some time, if sulphur or alkaline sulphides are present, there appears a red colouration from the reduction of nitro-benzol. The inverse reaction can be used for the detection of nitro-benzol.

Preservation of Sulphuretted Hydrogen Solution.

By adopting an artifice first proposed by Mr. Lepage, sulphuretted hydrogen solution can be kept for 12 or 15 months with scarcely any loss of strength. Instead of using water, saturate a mixture of pure glycerine and water with sulphuretted hydrogen gas and use it in the ordinary manner. This liquid dissolves rather less sulphuretted hydrogen than distilled water does, but none of the reactions are interfered with in the least, whilst the solution possesses almost perfect stability. Glycerine likewise prevents solution of ammonium sulphide from becoming coloured.

Obtaining Sulphuretted Hydrogen in the Laboratory.

E. Divers and Tetsukichi Schmidzu obtain a regular stream of pure hydrogen sulphide by gently heating a solution of magnesium hydrosulphide. Ordinary hydrogen sulphide (from ferrous sulphide and hydrochloric acid) is passed into water containing magnesia in suspension. The gas is absorbed, and the magnesia dissolves. The

decanted solution is colourless, and when heated to 60°–65° evolves a steady steam of hydrogen sulphide, free from hydrogen and hydrogen arsenide. The magnesia which is precipitated during the evolution of the gas can be re-converted by cooling and passing hydrogen sulphide into it.

Anomalies in the Detection of Sulphuric Acid.

In testing for sulphuric acid in the presence of phosphoric acid, attention must be directed to a remarkable case of interference which appears to have escaped observation until it was pointed out by Mr. Spiller.

If to an aqueous solution of glacial phosphoric acid a small proportion of sulphuric acid be added, the mixed liquid does not give the usual indication of a precipitate on adding a few drops of barium chloride, but requires a liberal addition of the last-named reagent in order to induce the formation of the sulphate. By adding dilute hydrochloric acid, or by raising the temperature of the clear barytic solution, the formation of a precipitate is determined; but continued ebullition fails, in many instances, to separate the whole of the barium sulphate. When, however, by the action of heat and of hydrochloric acid conjointly, the white precipitate makes its appearance, it is always found to be markedly different in physical character from the product usually obtained, being thrown down in the form of a semi-transparent flocculent precipitate, very like that obtained through the intervention of an alkaline citrate, as described in Mr. Spiller's paper, entitled 'On the Influence of Citric Acid on Chemical Reactions,'¹ read before the Chemical Society.

This remarkable property of obscuring the indication of sulphuric acid appears to be possessed only by the glacial modification of phosphoric acid; for, if the white flakes of phosphoric anhydride (as obtained by the combustion of phosphorus) be dissolved in water, no such result is apparent; nor do the hydrochloric acid solutions of bone-ash and of the ordinary sodium phosphate mask, in any appreciable degree, the presence of sulphuric acid. But if by heat the ordinary crystals of sodium phosphate be converted into pyrophosphate, and then dissolved in dilute hydrochloric acid, a solution is obtained which in this particular exactly resembles the glacial modification of phosphoric acid.

Detection of Free Sulphuric Acid in Vinegar.

Boil about 50 c.c. of the acid to be tested in a retort with a very small quantity of starch, until half the liquid is distilled; after it has cooled add a drop of tincture of iodine. If, under these circumstances, a blue colouration be produced, no sulphuric acid is present. If the blue colour does not appear, it may be concluded that sulphuric acid

¹ See the *Chemical News*, vol. viii. p. 280.

is present, which, by reacting on the starch, will have transformed it into glucose. With tincture of iodine, glucose gives no particular colouration.

Volumetric Estimation of Sulphuric Acid.

Prepare a standard solution of lead nitrate containing 33·1 grammes in each litre. This lead solution is added to the fluid containing the sulphuric acid in such proportion as to allow a slight excess of lead, after which the precipitate is filtered and washed, and the filtrate mixed with sodium acetate, and the excess of lead estimated by means of a standard solution of potassium bichromate, according to the process described at page 347. The lead precipitate is far preferable to the barium precipitate, as it subsides readily, filters clear, and is easily washed. Every cubic centimetre of the above lead solution requires 0·008 gramme of sulphuric acid for precipitation.

Lead sulphate is slightly decomposed by potassium bichromate; it is therefore necessary to remove it by filtration, before the excess of lead can be estimated. The quick and complete deposition of this precipitate enables us, however, to remove, by means of a pipette, a certain portion of the clear fluid, and to estimate the amount of the lead it contains, and calculate the whole without any filtration at all. There is no doubt that most sulphates may be analysed in this way; ammonia iron alum, copper sulphate, magnesium sulphate, each give very accurate results when subjected to trial; iron acetate alone, on account of its red colour, occasions some inconvenience in well observing the silver reaction.

Should, however, the base occasion some inconvenience—as, for instance, in calcium sulphate—it may be removed by boiling with sodium carbonate and the sulphuric acid estimated as usual in the filtrate.

Hydrochloric acid is the most troublesome of the acids, as in concentrated solutions lead chloride as well as sulphate is precipitated; and as mixtures of sulphates and chlorides frequently occur, it is necessary to add to these nitric acid, to evaporate them to dryness, and to expel in this way every trace of chlorine. Weaker acids, such as hydrosulphuric acid, are thereby also expelled.

Another method, simpler, but not quite so accurate, for the volumetric estimation of sulphuric acid is the following:—The solution is coloured with litmus, and very carefully neutralised; a solution of barium chloride of known strength is added in excess, and all the sulphuric acid thereby precipitated. Next, a titrated solution of sodium carbonate is added, in order to precipitate the excess of barium; and then, again, the excess of sodium solution used is estimated, volumetrically, by means of titrated dilute sulphuric acid. During these operations no salt is formed which can injure the colour of the litmus. In case salts are present in the original solution, the bases of which

could be precipitated by sodium carbonate, that precipitation is performed previous to the addition of soda. The filtrate, which contains the sulphuric acid combined with sodium, is neutralised, and again volumetrically titrated. The solutions required for this experiment are:—A solution of barium chloride, containing 52 grammes to the litre of water; a solution of sodium carbonate, containing 26.5 grammes of this salt to the litre of water; a solution of sulphuric acid, containing 20 grammes of monohydrated sulphuric acid to the litre of water. These solutions agree among each other, drop for drop. The advantage claimed for this method by its author, Dr. Clemm, is the non-necessity of having to wash out the barium sulphate and carbonate, and also that titration does not take place in a fluid rendered turbid by suspended barium sulphate, which always tends to render the observation of the colouration of litmus difficult.

For the volumetric estimation of sulphuric acid Dr. Haubst gives the following process, which enables one in a few hours to ascertain accurately the quantity of sulphuric acid combined with fixed alkalies and with earthy metals.

As water charged with alkaline carbonates cannot have any other salts of earthy metals but carbonates, all the sulphuric acid present is consequently in combination with alkalies. The standard solutions employed are centinormal oxalic or sulphuric acid, and, if thought necessary, centinormal ammonia.

The process is divided into two operations:—Estimation of sulphuric acid in the alkaline sulphate; then estimation of the whole sulphuric acid, the difference being that in combination with earthy metals.

Take 100 c.c. of the water (if sodium and potassium carbonates be present, neutralise with dilute hydrochloric acid); add a slight excess of baryta-water; then pass in a current of carbonic acid gas, or mix with it water highly charged with this gas; let it boil for a few minutes, and filter. The precipitate is washed with boiling water till the washings are neutral to test-paper, and the filtrate, which contains now the alkalies as carbonates, is titrated with the above-mentioned centinormal oxalic or sulphuric acid.

The amount of acid consumed is exactly the same as that originally combined with potash and soda. Lime and magnesia salts having been precipitated as carbonates cannot interfere with the process.

Simultaneously with the first operation the second part may be carried on. The same number of cubic centimetres is taken, raised to boiling, sodium carbonate added till the liquid remains distinctly alkaline. It is then, after some minutes' ebullition, passed through a small filter and well washed. All the sulphuric acid present is now in combination with potash and soda; lime and magnesia salts, having been converted into carbonates by the action of sodium carbonate, are filtered out.

Estimating Free Sulphuric Acid in Superphosphates.

The following method is recommended by Dr. R. Carter Moffat as being very accurate :—An aqueous solution of the superphosphate being made, evaporate slowly until a small quantity only is left ; add about 7 volumes of concentrated alcohol, and allow it to settle in the cold for some hours. This precipitates all sulphates, and leaves in solution, besides phosphates, the free sulphuric acid. Filter, wash with alcohol, add a large amount of water to the solution, carefully evaporate off the spirit, and estimate the acid in the usual manner by precipitation with barium chloride. The soluble phosphates do not in any way interfere.

Should a more ready, though less accurate, process be required, an aqueous solution of the superphosphate treated with a very dilute normal solution of ammonia gives tolerably fair results.

Precautions in Precipitating Barium Sulphate.

It is well known that precipitated barium sulphate may retain alkaline salts in quantities of from 1·5 to 2 per cent., which cannot be removed by the most careful washing. Stolba obtains the barium sulphate pure by digesting it (after washing until the wash-waters no longer show the reaction of barium) with 40 to 50 c.c. of a cold saturated solution of neutral copper acetate and some acetic acid, at nearly a boiling heat for 10 or 15 minutes. During the digestion, enough acetic acid must be present to prevent the formation of basic salt on boiling. Should basic salt form, which may be readily perceived at the bottom of the vessel, more acetic acid must be added, and the digestion must be renewed for 10 or 15 minutes. During the process, the vessel containing the precipitate should be constantly agitated. The alkaline salts retained by the barium sulphate undergo double decomposition with copper acetate, and the resulting products all admit of entire separation from the precipitate by means of hot water. The precipitate is washed until no reaction for copper is manifested on testing the washings with potassium ferrocyanide. This method is also satisfactory for the estimation of sulphuric acid in presence of a large excess of barium nitrate and chloride.

The commercial crystallised copper acetate is purified from sulphuric acid, and at the same time saturated with barium sulphate, by adding to its boiling solution a slight excess of barium chloride and acetic acid, and filtering from the precipitate.

Fresenius describes a number of very important experiments concerning the influence of various acids and salts on the precipitation of barium sulphate, and the admixtures of foreign salts with the precipitate. His conclusions are :—(1). Barium sulphate does not require 48,000 parts of water for solution as usually stated, but upwards of 400,000 parts, even in presence of hydrochloric acid, which slightly

raises its solubility. (2). Sodium chloride, potassium chloride, and barium nitrate do not increase its solubility very perceptibly, but the alkaline nitrates do so. (8). Hydrochloric acid does the same, and it must, therefore, be evaporated or partially neutralised before the precipitation. (4). Sodium chloride does not produce any foreign admixture in the precipitate. (5). Potassium chlorate does cause such admixture in a high degree. The precipitate can, however, be purified by digesting with hot hydrochloric acid, evaporating the same, and washing with water. (6). Sodium, potassium, and barium nitrate cause a very impure precipitate, which cannot be purified by washing with hydrochloric acid, but only by fusion with sodium carbonate, and estimating the sulphates in the aqueous solution of the fused mass.

Purification of Sulphuric Acid from Arsenic.

Arsenic almost always exists in commercial sulphuric acid in the form of arsenious acid, which being volatile, distills over with the sulphuric acid, and prevents its purification by rectification. If, however, previous to distillation, the arsenious acid is oxidised to the form of arsenic acid, which is non-volatile, the sulphuric acid which comes over on distillation will be quite free from arsenic.

MM. Bussy and Buignet recommend that a sulphuric acid which contains arsenious acid should be boiled with nitric acid, to oxidise arsenious acid to arsenic acid, then mixed with a little ammonium sulphate to destroy the excess of nitrous compounds, and distilled with precautions to prevent any particles being carried over by projection. The distillate will be free from arsenic.

As there is some theoretical danger that the ammonium sulphate might reduce the arsenic acid to arsenious, which would pass over as before, M. Blondlot recommends that manganese peroxides should be used to oxidise the arsenious acid. The way he proceeds is as follows : Manganese peroxide is added in the proportion of 4 to 5 grammes to the kilogramme of sulphuric acid, and the mixture heated to boiling in a porcelain dish, stirring all the time. It is allowed to cool, and is then transferred to a retort and distilled.

Maxwell Lyte employs a different mode of purification, chiefly with a view to ensuring the complete absence of all nitrous products, and obtaining a pure acid from the very first, and of thereby obviating the necessity of changing the receiver—a most dangerous operation when distilling sulphuric acid. If the acid contains nitrous compounds, heat it in a porcelain capsule to a temperature of about 110° C., with a small portion of oxalic acid, till the latter is completely decomposed and all effervescence has ceased ; about 0.25 to 0.5 per cent. is amply sufficient for nearly all samples of commercial acid. It is best to add the oxalic acid before heating, and to stir constantly till the reaction is completed. Now allow the acid to cool down to about 100° C., and add to it a solution of potassium bichromate in sulphuric acid, or

some of the salt itself in fine powder, until the pure green colour at first produced by the formation of chromium sesquioxide is replaced by a yellowish green, indicating an admixture of chromic acid in the free state. The acid so prepared, being now distilled, passes from the first perfectly free from all impurity. The addition of the bichromate has another advantage, viz. that if it be first of all applied to a small sample of the commercial acid, it indicates the presence of free sulphurous acid as well as of arsenious acid, and either of these being present, we may presume on the absence of nitrous compounds.

No doubt permanganates would answer equally well; but the potassium bichromate, which is cheap and easily procured, is so convenient as to leave nothing to be desired.

Detection of Gaseous Impurities in Sulphuric Acid.

It is essential for some purposes that oil of vitriol should contain neither sulphurous acid nor any of the lower nitrogen oxides; both of these impurities are met with in some commercial samples of oil of vitriol. Mr. R. Warington gives the following method for testing for the presence of sulphurous acid and nitrogen oxides.

About 2 pounds of the oil of vitriol are placed in a bottle, which the liquid half fills; the bottle is then stoppered and violently shaken for a minute or two. The gases contained in the oil of vitriol are thus washed out by the atmospheric air contained in the bottle. Sulphurous acid is then tested for by introducing into the air space of the bottle a slip of paper coloured blue by iodine and starch; the paper is conveniently held in the bottle by means of a wire and a cork. The bleaching of the paper gives evidence of the presence of sulphurous acid.

The test-paper is best prepared from Swedish filter-paper; this is first passed through a well-made solution of starch and then dried. A slip of this paper is next placed in a weak aqueous solution of iodine, where it remains till it has acquired a distinct blue colour. It is then removed, pressed between blotting-paper, and is now ready for use.

The paper thus prepared gradually loses its colour by exposure to air; it should therefore be used as soon as made; for the same reason its exposure to the gas in the bottle should not exceed 2 or 3 minutes; no perceptible change of colour will occur in this time if no sulphurous acid be present. The colour of the paper is also at once destroyed by heat; it cannot therefore be used for testing the gases given off by hot liquid.

The nitric oxides are detected by substituting for the first test-paper one imbued with potassium iodide and starch. As N_2O_2 forms N_2O_4 on contact with air, and N_2O_3 produces the same compound on contact with air and moisture, the presence of either of these three oxides will suffice to liberate iodine on the moist test-paper and colour the starch. Since sulphurous acid destroys the blue starch iodide, the

presence of an excess of this gas will prevent the detection of the nitric oxide. The nitric oxide is, on the other hand, without effect on the test-paper employed for the sulphurous acid. If, therefore, the sulphurous acid is not in excess, it is quite possible to obtain the reactions of both gases from the same sample of oil of vitriol, and this is no uncommon occurrence with oil of vitriol which has been imperfectly boiled.

In using the reaction here described for the purposes of general testing, it is to be remembered that sulphuretted hydrogen produces the same effect as sulphurous acid.

Analysis of Sulphuric Anhydride and Fuming Sulphuric Acid.

O. Clar and J. Gaier weigh the fuming acid in thin glass bulbs of 20 millimetres in diameter, provided with two long capillary points opposite to each other. The bulbs are half filled with the acid by suction, and are then sealed up at both ends. After weighing, a point is broken off under water. The anhydride is weighed in small glass bottles 58 millimetres high, 17 millimetres wide, with high ground stoppers, enlarged conically above, and with a small aperture in its summit closed with a minute glass plug. The interior of the stopper is filled with glass wool, slightly moistened. The bottle when charged and weighed is allowed to glide in an inverted position into a 2-litre flask held in a sloping position, and containing about 500 c.c. water at 50° to 60°. After mixture has taken place through the small aperture in the stopper, the liquid is made up to 1 litre, and a portion of 100 c.c. is titrated with 5-normal soda.

Detection of Sulphurous and Thiosulphuric Acid.

Instead of employing hydrochloric acid and zinc, aluminium and hydrochloric acid are preferable. Zinc may be contaminated with sulphur compounds, while aluminium is always pure in this respect; the latter metal, moreover, dissolves very slowly in dilute hydrochloric acid, and, therefore, the same piece of aluminium may serve for many testings. Dr. Reichardt has distinctly detected the sulphuretted hydrogen when a solution of one part of sulphurous acid in water, diluted with 500,000 parts of water, was treated with hydrochloric acid and aluminium.

Estimation of Sulphites and Hydrosulphites.

If both salts are present together in solution, it is necessary to find the quantity of iodine which a part of the liquid requires if mixed with acetic acid, and the quantity of barium sulphate which an equal part of the solution yields after complete oxidation with bromine. Two equations are thus obtained with two unknown quantities. If a sulphate is also present its quantity is ascertained by adding to the

liquid sodium bicarbonate, passing a current of carbonic acid through the liquid, heating after expulsion of the air, and, after the addition of hydrochloric acid in excess, concentrating to a quarter its volume. The sulphurous acid being thus expelled, the sulphur is filtered off, and the sulphuric acid in the filtrate is estimated in the ordinary manner. For the estimation of sulphurous acid in air, B. Proskauer passes a known volume of air through 50 or 75 c.c. of a solution of permanganate containing 15 grammes of the crystalline salt per litre, and 2 or 3 c.c. of hydrochloric acid. The solution is placed in a Bunsen bulb tube.

PHOSPHORUS.

Detection of Phosphorus.

When previously well-dried (previous ignition is often required) inorganic combinations of phosphorus are ignited in a pulverised state in a test-tube with small quantities of magnesium wire, ribbon, or powder, there is formed magnesium phosphide. After cooling, the fused mass, on being moistened with water, will disengage phosphuretted hydrogen gas, which, in many instances, will be found to be the spontaneously inflammable variety. Phosphorus may be detected in the same way in organic substances—as, for instance, brains, muscle, &c.—but these should be previously calcined, and the dry animal charcoal so obtained submitted to the experiment.

For the detection of phosphorus in organic liquids, the following modification of Mitscherlich's process will be found to answer well. In this process the presence of phosphorus is established by the phosphorescence imparted to the aqueous vapours on distilling the liquid or liquefied mixture, and the distillation of the phosphorus is increased by the addition of sulphuric acid, sodium chloride, sugar, &c., whereby the boiling-point of the liquid is made to approach that of phosphorus.

In the place of Mitscherlich's apparatus, the following more simple one is proposed; it is easily prepared and readily taken apart. It consists of an ordinary flask, connected with a receiving-bottle by means of a glass tube, which passes about 18 inches through a glass cylinder filled with cold water. A long straight tube conducts the gaseous products from the bottle. The lamp and flask, and about three-fourths of the glass cylinder, are surrounded with dark paper. The operation is best performed in a dark room.

The phosphorescence of the liquid increases in intensity with the consistence of the liquid and the quantity of the phosphorus. The gas-bubbles are luminous, rise in the mixture, and apparently burn upon its surface with a bright flame. With the temperature the light increases; a photosphere fills the flask, rises in the tube, and moves up and down within the cooled part. Sometimes only a column or a luminous ring appears stationary at the point where the vapours are cooled, and a luminous fog or sparks gradually sink into the receiver,

or a sudden, frequently-repeated flash of light is observed. If the heat is raised too high, or the cooling is insufficient, the phosphorescence passes through the long gas-tube, at the mouth of which the gases take fire, if the volatile oils from *Crucifera* (mustard, &c.) have been present.

Coffee, mustard, smoked meat, highly-seasoned food and beverages, and medicines containing odorous gum-resins, volatile oils, musk, camphor, chlorine, &c., have the property of covering the odour of a small portion of phosphorus.

The reaction is not interfered with by the presence of ipecacuanha, tartar emetic, magnesia, hydrated iron oxide, musk, castor, opium, albumen, neutral, acid or basic salts and double salts, volatile organic acids, chlorides, iodides and sulphides, and free acids; but iodine, and mercury chloride, and bichloride in considerable proportion, and metallic sulphides in the presence of free sulphuric acid, and particularly *oleum cinæ* (*Artimisiæ*), interfere with or prevent the reaction.

Numerous experiments, by distilling the brain of various animals, blood, albumen, casein, fibrin, legumin, and other protein compounds, with dilute sulphuric acid, have not yielded the least phosphoric reaction.

Detection of Arsenic in Commercial Phosphorus.

In preparing dilute phosphoric acid by the oxidation of commercial phosphorus, the precaution should be taken to pass a current of sulphuretted hydrogen through the solution, in order to free it from all substances precipitable by that agent from acid solutions; by this operation arsenic sulphide is frequently thrown down. In order to estimate the amount, Dr. C. J. Rademaker oxidised 100 grammes of phosphorus with nitric acid, diluted the solution and precipitated the arsenic as sulphide, by means of sulphuretted hydrogen; the solution was allowed to rest for six days, after which the precipitate was collected on a filter and washed, transferred to a small evaporating-dish, oxidised with nitric acid, reduced by means of sulphurous acid to arsenious acid, again precipitated by means of sulphuretted hydrogen; the precipitate digested with ammonia to free it from adhering sulphur, the solution filtered, evaporated, dried, and weighed, when it was found to amount to nearly 1 gramme of arsenic sulphide.

Phosphorus Holder.—Mr. E. Kernan gives the following ingenious method of making a phosphorus crayon which is perfectly safe in the hand for lecture experiments in luminous writing, &c.:—A few inches of lead tube, $\frac{1}{4}$ in. bore, are contracted to an open cone at one end. As much phosphorus as one may choose is put into the cone of the tube; the phosphorus is made to project slightly from the cone; the upper part of the tube is filled with water and corked. To put in the phosphorus, as much as may be required is melted in a conical glass, or test-tube, the cone of which is larger than that of the

lead tube. This is put standing in the melted phosphorus, which fills the cone and tube to its own outside level. When cold, there is a nice projecting crayon, from the form of the glass. Any phosphorus outside the lead tube may be melted off. To renew the writing-point, a test-tube, conical below, is fitted to the cone of the lead: the whole is held in warm water for a minute, when sufficient phosphorus flows out to form a new point.

Preparation of Phosphuretted Hydrogen.

Prepare zinc phosphide by mixing together amorphous phosphorus with half its weight of powdered zinc, and gently heating the mixture in a hard glass tube through which a current of dry hydrogen or coal-gas passes. The tube and contents must be cooled in the current of gas. From the zinc phosphide so prepared phosphuretted hydrogen may be readily obtained by means of dilute sulphuric acid or by boiling with caustic potash. The gas is, however, the non-spontaneously combustible kind. The spontaneously combustible gas may be obtained by taking a larger quantity of zinc phosphide and dissolving it in warm dilute sulphuric acid.

Distinction between Phosphates and Arseniates.

Mr. A. H. Allen remarks that it is well known that the difference in colour between silver phosphate and silver arseniate furnishes the most simple means of distinguishing between the two classes of salts. The presence of free nitric acid or ammonia interfering with the reaction, it is necessary to apply the test to a neutral solution, in which case many other salt radicles may be precipitated. If the phosphate or arseniate be first separated as the ammonio-magnesium salt, it is usual to dissolve this precipitate in nitric or acetic acid before adding silver nitrate. This is quite unnecessary, the characteristic yellow phosphate or brown arseniate being immediately produced on addition of silver nitrate to the crystalline precipitate. This modification renders the test more delicate as the reaction takes place in a neutral liquid. A few streaks on a test-tube show the reaction very distinctly, hardly changing colour if due to phosphate, but turning quite brown if caused by arseniate, in each case becoming soluble in ammonia. On this account the ammonio-magnesium salt must be washed free from ammonia, which would either prevent the reaction or lead to confusion by precipitating brown silver oxide. Acetic acid dissolves both silver phosphate and arseniate, the former far more readily than the latter. If, therefore, acetic acid be gradually added to a mixed precipitate of silver phosphate and arseniate, the phosphate dissolves first, and the brown colour of the arseniate becomes more apparent. If, after addition of a moderate quantity of acetic acid, the liquid be filtered, the dissolved phosphate may often be detected by cautious neutralisation with ammonia, when the yellow silver

phosphate is thrown down; but this reaction is uncertain, as both silver phosphate and arseniate are soluble in ammonium acetate, the phosphate more readily than the arseniate.

Estimation of Phosphoric Acid.

A. By the Modified Tin Process (Reynoso's).—This method depends upon the fact that, when metallic tin is added in excess to a solution of a phosphate in nitric acid, the stannic acid formed by the oxidation of the metal combines with the phosphoric acid and completely removes it from solution. On filtering, therefore, we at once separate the bases which remain in solution from the insoluble combination of stannic and phosphoric acids. In order to estimate the amount of phosphoric acid contained in the tin oxide, the compound is dissolved in a small quantity of concentrated potash solution, when the two acids dissolve as metastannate and potassium phosphate; the fluid is now saturated with sulphuretted hydrogen, a small quantity of ammonium pentasulphide added, and, lastly, a slight excess of acetic acid. The tin sulphide is then separated by filtration; all the phosphoric acid is contained in the filtrate, and its amount may be estimated by the ordinary method as magnesium ammonio-phosphate. Two very good modifications of this method have been given.

Modification 1.—According to the first the substance is dissolved in nitric acid. When there are any difficulties in getting it into solution, dissolve it first in any convenient agent, then add excess of ammonia to the solution, which precipitates all the phosphoric acid, with most of the bases; well wash this precipitate; it will then be readily soluble in nitric acid.

If, for instance, a specimen of cast-iron is being analysed, it must be dissolved in aqua regia; if a refractory mineral, it must be attacked by alkalies, &c.

The nitric solution having been obtained (which should be free from chlorides), throw into it an indefinite quantity of pure tin; about four or five times the supposed weight of the phosphoric acid present may be employed. This tin passing to the state of stannic acid, under the influence of the nitric acid, carries down with it all the phosphoric acid, as well as a great portion of the iron and a little aluminium; wash at first by decantation and then on a filter, and place on one side the nitric solution, which is free from tin, but contains all the bases minus a portion of iron and aluminium. Then redissolve the precipitate in a small quantity of aqua regia, and, without troubling about the filaments of filter-paper, or the small portions of tin phosphate which may remain undissolved, supersaturate with ammonia, and then add an excess of ammonium sulphide. The stannic acid and tin phosphate immediately dissolve, leaving a black precipitate of iron sulphide containing aluminium; allow it to stand for an hour or two, and then filter, taking care to wash the precipitate with ammo-

nium sulphide to remove the last traces of tin. It is then only necessary to add magnesium sulphate to the filtered liquid to obtain the characteristic precipitate of magnesium ammonio-phosphate. Collect this on a filter, wash it first with ammonium sulphide, then with ammoniacal water, and afterwards calcine in the ordinary manner.

The filter containing the iron sulphide and aluminium is redissolved in nitric acid, and the filtered liquid is added to the original solution of the bases, which may then be separated in the ordinary way.

This method is both simple and rapid ; it enables one to estimate the phosphoric acid contained in the most complicated mixtures, and then admits of the accurate separation of the bases.

Modification 2.—Obtain the phosphate in solution in nitric acid, as described above. Concentrate the solution and add the strongest nitric acid (boiling at 86°C.). The nitric acid solution is now in the highest possible state of concentration : on throwing a small quantity of tin into this solution, the metal is rapidly oxidised to stannic acid, and the supernatant liquid remains perfectly clear. The preliminary heating of the solution is indispensable, since in the cold the metal is apt to become passive, when it completely resists the action of the acid. The precipitate is now dissolved in a small quantity of caustic potash, and saturated with sulphuretted hydrogen ; on adding acetic acid in slight excess the tin-sulphide is precipitated. The precipitate is then separated by means of the Bunsen filter-pump, and the whole of the phosphoric acid is contained in the filtrate. After concentrating the solution, and again filtering from a minute precipitate of tin-sulphide, which invariably separates out (tin-sulphide being slightly soluble in solutions containing sulphuretted hydrogen), the phosphoric acid may be precipitated as the magnesium-ammonio salt, and weighed as pyrophosphate.

The amount of tin need not exceed four times the weight of the phosphoric acid present. This, however, is the minimum quantity that can be used with safety.

B. Estimation of Phosphoric Acid by the Magnesium Process.—The estimation of phosphoric acid in minerals containing fluorine, iron, and aluminium is a matter of considerable difficulty. After dissolving in mineral acids, most authorities advise that the acid solution should be brought to dryness before proceeding to separate the calcium. Some analysts, however, neglect this part of the process, from the impression that it has no influence on the estimation of the phosphoric acid, and that it is only necessary when the siliceous matter is required for a full analysis. Mr. T. R. Ogilvie has instituted several experiments to show that this impression is an erroneous one. From them the following are selected :—

(1) A gramme of Cambridge coprolites was dissolved in moderately strong hydrochloric acid, evaporated to dryness, the residue again

dissolved in acid, the calcium separated with ammonium oxalate, citric acid added to hold up iron and aluminium, the solution made alkaline with ammonia, and the phosphoric acid precipitated with 'magnesia mixture.' A perfectly granular precipitate was obtained, which, after standing for twelve hours, was washed, dried, ignited, and weighed, and found to be equivalent to 47.44 per cent. tricalcic phosphate.

(2) Another gramme of the same coprolites was treated in exactly the same way, with the exception that the acid solution was *not* brought to dryness. The magnesium ammonio-phosphate, as it gradually formed, presented the usual appearance; but, when stirred up after a few minutes, a white flocculent body was also observed. After standing for the usual time, the whole precipitate was collected, washed, dried, ignited, and weighed, and gave 58.04 per cent. calcium phosphate.

(3) A third gramme was treated as in (2), with the difference that, after the addition of citric acid, the solution was made alkaline with ammonia, and allowed to stand. In a short time a white flocculent precipitate formed, which was filtered, washed, dried, ignited, and weighed.

To the clear ammoniacal filtrate, 'magnesia-mixture' was added; and a granular precipitate, free from any flocculent matter, was obtained, equivalent to 47.2 per cent. calcium phosphate. This closely corresponds with the result (*viz.*, 47.44 per cent.) obtained in (1) after evaporating to dryness.

The flocculent precipitate got by ammonia weighed 4.05 per cent. Had it not been removed, it would have been taken as magnesium ammonio-phosphate, and, as such, been equivalent to 5.66 per cent. calcium phosphate; this, added to 47.2 per cent., gives 52.86 per cent., against 58.04 per cent. found in (2) by weighing the flocculent precipitate along with the magnesium ammonio-phosphate.

In these experiments, care was taken that the calcium was perfectly separated, and that sufficient citric acid was present to hold up iron and aluminium.

The precipitate which forms on the addition of ammonia to the citric acid solution when the material has not, at the outset of the process, been brought to dryness, consists of silica, alumina, and iron sesquioxide as silicate, and, when carefully washed, is free from phosphoric acid. In the case of sombrerite, some magnesium ammonio-phosphate would also come down, owing to the presence of a considerable quantity of magnesium in that mineral. But, with coprolites and other phosphatic minerals, which contain only minute quantities of magnesium, neither phosphoric acid nor magnesium is found, unless the flocculent precipitate is not filtered from the solution for a few hours.

All phosphatic minerals which contain fluorine, iron oxide, and alumina give this precipitate.

Those minerals containing fluorine, and only a trace of iron and aluminium, such as Canadian apatite and Spanish phosphorite, give no appreciable flocculent precipitate. A sample of sombreroite was also examined, but, as it was exceptionally free from iron and aluminium, it gave no flocculent precipitate.

It may be mentioned that, when coprolite, or other ferruginous phosphatic mineral, is moistened with sulphuric acid, gently heated, and the fluosilicic acid which forms driven off, then dissolved in hydrochloric acid, and the calcium removed without the solution being brought to dryness, no flocculent precipitate is obtained.

It would thus seem that, in the analysis of the majority of the phosphatic minerals at present in use by manure manufacturers, special care must be taken to obtain a pure and perfectly granular precipitate of magnesium ammonio-phosphate, either by evaporating the acid solution to dryness, or by separating the precipitate which forms on the addition of ammonia to the solution containing citric acid; otherwise an erroneously high result is obtained.

For the rapid estimation of phosphoric acid, magnesia, and lime, M. G. Ville proceeds as follows:—Attack in the cold 2 grammes of phosphate with 50 c.c. of hydrochloric acid or weak nitric acid, and filter it. Take 5 c.c. of this solution, add at first some citric acid, then ammonia in excess, and lastly precipitate by a solution of magnesium chloride, the liquid being maintained ammoniacal.

The phosphoric acid deposits in the form of magnesium ammonio-phosphate. By means of the exhausting filter (Figs. 9, 10), separate it from the supernatant liquid, wash it with ammoniacal water, exhaust again, and finally estimate the precipitate by means of uranium acetate, according to Leconte's process.

Suppose we have to analyse calcium superphosphates of commerce. The necessity of distinguishing phosphoric acid which is in the soluble state from that which is in the insoluble state, requires two parallel attacks, one with distilled water and the other with weak nitric acid. The operation is always the same. Work on each liquid separately, as just pointed out in the case of natural phosphates.

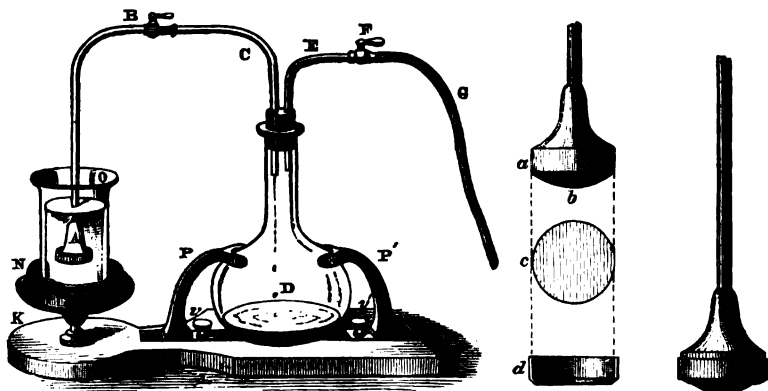
A glance at the accompanying drawing of the apparatus that has so much expedited the work is sufficient to understand the arrangement and mode of action. (Figs. 9 and 10.)

An exhaustion is formed equal to some centimetres of mercury in the globe, D, by the help of a small hand-pump. The base of the cone, A, *a*, *b*, covered with one or two discs of blotting-paper *c*, held in place by a ring, *d*, fitting tightly by friction, works as a true filter, which acts under pressure.

Two forms of apparatus have been made, one of platinum (Fig. 9), and the other of glass (Fig. 10). The fragility of the latter is obviated by means of the consolidation arm, M, which firmly fixes the exhausting tube.

In order to render the precipitation almost instantaneous, it is necessary to operate on a moderate quantity of phosphate, and to employ an excess of magnesium chloride. With a small quantity of

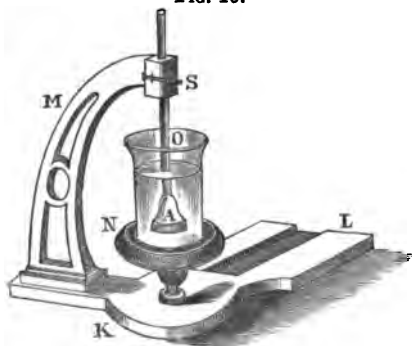
FIG. 9.



chloride the precipitation is slow, with an excess it is immediate. After waiting a quarter of an hour, we may proceed with the estimation of phosphoric acid, only the filtration takes a little longer; after an hour the result is perfect.

An excess of ammonium citrate holds in solution very appreciable

FIG. 10.



quantities of magnesium ammonio-phosphate; the loss, however, which results from it is very slight. For 0.05 gramme of phosphoric acid, and after waiting 18 hours, not less than 6.852 grammes of citric acid were required to retain in the solution 0.002 gramme of the phosphoric acid. When the quantity of citric acid employed is from 80 to 100 times that of the phosphoric acid, there is no

loss. On the contrary, the presence of lime completely changes the results.

Calcium citrate dissolves nearly three times more magnesium ammonio-phosphate than does ammonium citrate. The intervention of 0.059 gramme of lime has sufficed, in fact, to raise the loss of phosphoric acid from 0.002 gramme to 0.006 gramme; but an excess of magnesium chloride, so efficacious in hastening the precipitation of the magnesium ammonio-phosphate, completely neutralises the solvent

action of the calcium and ammonium citrates, and confers on the results both accuracy and concordance.

Mr. T. R. Ogilvie finds that the magnesia process for the estimation of phosphoric acid combined with alkalies is perfectly trustworthy and accurate when a moderate excess of magnesia-mixture is used.

The estimation of phosphoric acid, combined fully with lime only, as magnesium ammonio-phosphate, is not satisfactory under any conditions. It will yield a low result when a moderate excess of magnesia-mixture is used, owing to the solvent action of the ammonium oxalate introduced in the act of removing the alkaline earth; or a high result when a greater quantity of magnesia-mixture is used.

The estimation of phosphoric acid, combined with lime and iron and alumina oxide as magnesium ammonio-phosphate, is also unsatisfactory, owing to the combined action of ammonium oxalate and ammonium citrate. High or low results may be got, according to the quantities of these salts and of magnesia-mixture present.

Precipitation in boiling solution, or re-precipitation, will not fully remedy the errors incident to the use of the reagents mentioned.

By the judicious use of the reagents the least error that may be anticipated in the estimation of calcium phosphates by this process is 1.27 per cent., and in the estimation of phosphates containing iron and alumina oxide 1.01 per cent., while, by the indiscriminate use of reagents, errors up to 10 per cent. or 12 per cent. may be introduced.

As to the special result of this investigation, Mr. Ogilvie condemns the use of this process in the analyses of phosphates containing iron and alumina, unless in cases in which the results are expected to be merely *closely approximate*. In all analyses that are to be the basis of money valuation or of scientific statements, the molybdate or other method should certainly precede precipitation with magnesia.

Prof. Tollens states that if a precipitate of magnesium ammonio-phosphate is contaminated with magnesium or calcium triphosphate, caustic lime, or magnesia, or the citrates of these bases, there is obtained on ignition a white mass, which, if covered with silver nitrate and heated quickly, turns yellow. This test should be especially applied when citric solutions of phosphates are directly precipitated with magnesia-mixture.

M. Joulie uses the following modified magnesia process. He employs as a precipitating solution—

Citric acid	400 grammes
Magnesium carbonate	20 „
Distilled water	200 „

When the magnesium carbonate is quite dissolved, 500 cubic centimetres of ammonia at 22° Beaumé are added. The liquid becomes hot, and the rest of the citric acid dissolves. It is allowed to cool, and is

made up to the volume of a litre with distilled water, filtering if needful. The solution is permanent; it is decidedly acid, but only heats slightly when mixed with a large excess of ammonia. The precipitate thrown down by this liquid is redissolved on the filter with dilute nitric acid, re-precipitated with ammonia, collected and again washed, ignited and weighed.

An equally accurate result may be obtained with greater speed by estimating the phosphoric acid contained in the precipitate volumetrically by means of a standard solution of uranium nitrate.

Dr. Carl Mohr remarks:—This method of treatment introduces into the solution too large a quantity of neutral ammoniacal salts, which are known to have a retarding effect on the appearance of the final reaction with potassium ferrocyanide. It is also known that large quantities of neutral calcium and alkaline salts have the same disturbing influence, rendering the results always too high. It is hence of great importance, in estimations with uranium, to keep within the boundaries which were observed in standardising the solution. This state of affairs has led the author to obtain a double standard for his uranium solution; the one for solutions poor in lime, such as superphosphates, Mejillones' guano, &c.; and the other for solutions rich in lime, like the marl phosphates. The differences are not very considerable, but still enough to have a noticeable effect in the result. Thus for superphosphates 1 c.c. of the uranium solution represented 0.0041 phosphoric acid, but for marl phosphates only 0.0039 gramme.

The author has undertaken to estimate, by a series of comparative experiments, the influence of combined ammonia in titrating magnesium ammonio-phosphate with uranium, and also to decide in how far this ammonium compound has a retarding action upon the appearance of the final reaction. For this purpose he prepared a solution of pure calcium phosphate in dilute nitric acid. In one series of experiments portions of 10 c.c. of this solution were mixed with sodium acetate and titrated with uranium. In the second series the lime was thrown down with ammonium oxalate, and the phosphoric acid with magnesia. In both series equal quantities of uranium solution would be consumed if the ammonium compound had no disturbing influence.

In direct titration the average quantity of uranium solution consumed was 9.46 c.c. If the phosphoric acid was precipitated as magnesium ammonio-phosphate, dissolved and titrated, the average was 9.37.

These experiments prove that there is a sufficient agreement between the two processes if, in using the second or indirect method, the precaution is adopted of allowing the precipitate and filter to stand for some time in a warm place, so that the free ammonia of the washing water may evaporate.

Mr. E. W. Parnell considers that the correction of 1 milligramme

for every 54 c.c. of filtrate and washings is unnecessary, and that the two ammoniacal solutions should be raised to a boil before being mixed, to prevent an excess of the base from being carried down.

The Committee of the British Association are of opinion that magnesium sulphate should be abandoned in favour of the chloride.

The volume of magnesia-mixture employed for the precipitation should only be in moderate excess of the amount necessary to completely precipitate the phosphate present.

The use of a large excess of the precipitate causes a more rapid separation of the double phosphate, but is attended with such a serious tendency to error that any advantage gained is more than counter-balanced. The precipitation should be conducted in the cold. The proportion of free ammonia in the liquid should be large.

If the above precautions are duly observed, and silica, fluorine, iron, and aluminium be previously removed, it will rarely be necessary to purify the precipitate by solution in acid and reprecipitation with ammonia. In re-precipitating, some magnesia-mixture should be added, as its presence tends to reduce the solubility of the precipitate in the ammoniacal liquid.

In igniting the precipitate, the heat should be very gentle at first, and afterwards be raised as high as possible. If citric acid has been employed, the ignited precipitate is often discoloured. This may be remedied by cautious treatment in the crucible with strong nitric acid, followed by re-ignition.

If the precipitate of magnesium ammonio-phosphate be titrated by standard solution of uranium instead of being weighed, many of the above precautions are rendered superfluous.

Concerning the usual method of estimating magnesium ammonio-phosphate by ignition as magnesium pyrophosphate, Dr. Broockmann remarks that it involves certain sources of error which cannot be avoided, even with the utmost care. Such are the double salts creeping up the sides of the beaker and of the funnel, so that it is not readily brought into the filter without loss; then there is loss in the form of dust on introduction into the crucible; and, thirdly, there are variations in the ash of the filter. To avoid these sources of error the author dissolves the washed precipitate direct from the filter, and any particles present in the beaker, in nitric acid, places the solution in a weighed crucible, evaporates to dryness, and ignites.

C. Estimation of Phosphoric Acid by the Uranium Process.

In the analysis of manures, coprolites, bone-ash, and similar commercial substances, the magnesium process for estimating phosphoric acid is beset with so many difficulties that it is worth while to look for some other method by which the same end can be attained without the expenditure of so much time and trouble. Mr. Sutton strongly recommends the uranium process, which he considers to be equally accurate with the magnesium process, and far preferable to it in readiness of

application and general convenience. One of the chief advantages connected with the use of uranium as a means of estimating phosphoric acid in calcium phosphates, &c., is that the presence of acids does not interfere with the result.

The metals which admit of this mode of estimation are, so far as present experiments have proved, potassium, sodium, calcium, magnesium, iron, and aluminium; the two latter only, however, with modifications of the process as applied to the former. These modifications are given further on.

In the presence of potassium, sodium, magnesium, calcium, and barium, the following course must be adopted:—

The substance is to be dissolved if possible in acetic acid; if, however, this is not to be done, a nitric, hydrochloric, or sulphuric acid solution is admissible, taking the precaution to avoid any great excess of acid; add ammonia in excess, and redissolve the precipitate in acetic acid; in the presence of mineral acids it is advisable to add ammonium acetate as well as acetic acid. Lastly, add a solution of uranium acetate (best obtained by dissolving pure uranium ammonio-carbonate in acetic acid) and heat to boiling, by which means the phosphoric acid is completely separated as uranium and ammonium phosphate.

This precipitate is of a greenish-yellow colour and somewhat slimy in its nature; therefore in order to prevent the pores of the filter from being choked by it, it must be handled in the following manner:—After boiling, set aside on the sand-bath, and allow the precipitate to settle; when the supernatant liquid is clear, decant through the filter, pour water over the precipitate, and again boil for a few moments; decant as before, taking care that the precipitate has entirely subsided; repeat the process three or four times until the sliminess of the precipitate has given place to a feathery appearance, then pour it out upon the filter and complete the washing in the usual way.

The above process may be hastened somewhat by adding to the liquid in which the precipitate is first suspended, after it has somewhat cooled, a few drops of chloroform; then vigorously stirring the liquid or boiling it up once or twice causes the precipitate to settle more rapidly.

The uranium and ammonium phosphate thus obtained is totally insoluble in water and acetic acid, but easily so in mineral acids; the addition, however, of a sufficient excess of ammonium acetate throws it down completely again on boiling. On burning the precipitate the ammonia is driven off, and a lemon-coloured phosphate of uranium sesquioxide is obtained. If, however, carbon or any reducing gas is present during the burning of the precipitate it is partly reduced to phosphate of uranium protoxide, of a green colour; but on moistening it with nitric acid and again heating, the yellow colour of the higher oxide is reproduced.

It is therefore advisable in burning the precipitate to separate it

from the filter, first burning the latter, then adding the former, and heating to redness until every trace of carbon is removed. As a precaution against partial reduction it is advisable in all cases to moisten the precipitate when cool with nitric acid, and again heat to redness. The burning may take place in an open platinum crucible, and as the precipitate is scarcely hygroscopic it may be weighed uncovered.

If it should be necessary to redissolve the precipitate in order to estimate the phosphoric acid afresh, the solution must first be preceded by melting the precipitate with a considerable excess of sodium carbonate so as to convert the pyrophosphoric into tribasic phosphoric acid.

The composition of the uranium phosphate is as follows :—

		Per cent.
$2\text{U}_2\text{O}_5$	285.6	80.01
P_2O_5	71.0	19.99
	<hr/> 356.6	<hr/> 100.00

Therefore $\frac{1}{2}$ of the precipitate may be calculated as phosphoric acid.

This process has been used for the estimation of phosphoric acid in guanos, the so-called lime, bone-ash, coprolite, &c. superphosphates, in above a hundred analyses, and in many of them the results controlled by other methods, without one instance of inaccuracy or failure. In the more delicate process of urinary analysis it has been found equally reliable.

Special Precautions to be taken when Iron is present.—When a compound containing iron as well as phosphoric acid is submitted to analysis by the uranium process, the precipitate of uranium-phosphate invariably carries down a portion of iron with it. In this case the colour of the precipitate is altered to a dirty orange-yellow, and possesses a somewhat granular appearance. The quantity of iron depends in some measure upon the length of time the mixture has been kept at a boiling heat. If the boiling be continued for about 20 minutes, the iron is entirely removed from the precipitate, and the solution is coloured red by acetate of iron sesquioxide. The better way, however, is not to depend upon this mode of separation, but to reduce the iron sesquioxide to protoxide by means of uranium protochloride.

The compound is to be dissolved in the smallest possible quantity of hydrochloric acid (at most $1\frac{1}{2}$ ounces) and the solution of uranium protochloride added in sufficient quantity to produce a distinct green colour, or until one drop of potassium sulphocyanide does not show a change to red. Now add ammonia in sufficient quantity to neutralise the free hydrochloric acid, making sure by throwing into the mixture a small piece of litmus-paper. Add a solution of uranium acetate and free acid, together with a few drops of acetate of uranium protoxide (obtained by precipitating the protochloride with ammonia and redissolving in warm acetic acid), to ensure the presence of sufficient protoxide, and heat to boiling.

The mixture must now possess a distinct greenish colour, not a dirty tinge, which shows the presence of undissolved uranium protoxide. Put aside until the precipitate has settled; when this has *completely* taken place, decant the supernatant liquid through the filter; pour hot water over the precipitate, adding some ammonium chloride, and boil again; repeat the operation once more, and the washing is complete; the precipitate may now be thrown upon the filter, dried, and burned as described at the commencement of this process.

Preparation of Uranium Protochloride.—It may not be amiss here to give the best method of preparing a solution of uranium protochloride, which promises to be a most serviceable reducing agent in analysis.

Uranium ammonio-carbonate is to be dissolved in about twice as much hydrochloric acid (diluted with an equal quantity of water) as is necessary for solution. A concentrated solution of platinum bichloride is added in the proportion of about 2 drops to each ounce of uranium-salt; fine shreds of copper are then to be added in excess, and the mixture boiled for 10 or 15 minutes, or until the liquid assumes a distinct green colour, and the uranium sesquichloride is reduced to protochloride.

In order to remove the copper protochloride from the solution it is now to be boiled until, on adding a few drops to some water, an immediate precipitate is produced. Half an hour's boiling is generally sufficient to attain this end. The solution is then to be diluted pretty freely with water, and set aside to cool. When perfectly cold, the copper will in great measure be separated. Sulphuretted hydrogen, however, must be passed through the filtered solution till every trace of copper is precipitated and the liquid smells strongly of the acid.

The filtered liquid is now to be poured into a porcelain capsule, and evaporated at a boiling heat, adding some considerable quantity of ammonium chloride to prevent the precipitation of protoxide and uranium sulphide, which would otherwise be the case.

As the sulphuretted hydrogen is very difficult to remove, the evaporation must be carried on till the liquid corresponding to each ounce of the original uranium salt is reduced to about 3 ounces. It is absolutely necessary that every trace be removed. If at the end of the operation a precipitate has occurred, it may be dissolved in a little concentrated hydrochloric acid after the clear green liquid has been poured off, and the two solutions mixed and kept for use.

The solution so prepared contains ammonium chloride, which is of no consequence for the purpose here contemplated; neither is it any hindrance to the preparation of the pure crystals of uranium protochloride, as on adding excess of ammonia the uranium is precipitated and can be redissolved.

The value of this solution as a means of reducing sesquioxide to iron protoxide (and probably other higher oxides to lower) cannot be too highly estimated, for at ordinary temperatures it takes place speedily, but at boiling heat immediately: moreover, the change is visible to the eye, for the reddish colour of the solution gives place to green, and so long as this is the case the iron exists in the form of protoxide.

The delicacy of this reaction may be readily seen, if to a solution of iron sesquichloride a drop or two of potassium sulphocyanide be added, which produces a blood-red colour: add now a few drops of the uranium solution, and immediately the colour turns to green, showing that a reduction has taken place; this reaction may be made over and over again by adding first iron and then uranium.

Concerning the uranium method Mr. A. Kitchin remarks that the chief points required are a sufficient amount of ammonium acetate, and not too much free acid present; if these precautions are adopted the precipitate settles in a few minutes. The washing is best done first by decantation, boiling up after each fresh addition of water, and lastly on the filter. After drying, the precipitate is strongly ignited until the filter is consumed; then a little nitric acid added, evaporated to dryness, and finally gently ignited; the residue should be of a full yellow colour. If, in the final ignition, too much heat be applied, the uranic phosphate is reduced to a considerable extent, and turns a greenish colour; a second evaporation with nitric acid is then necessary.

M. F. Jean dissolves the phosphatic matter in nitric acid, and the solution, separated by filtration from insoluble matter, is mixed with a slight excess of ammonia. Citric acid is then added, which dissolves the precipitate formed by the ammonia, and yields a perfectly clear and acid solution, which is boiled for some time with uranium acetate. The yellowish precipitate formed is collected on a filter, washed with boiling water, dried, ignited, and weighed. It contains 20.04 per cent. of phosphoric acid. The filtrate on examination with ammonium molybdate is found free from phosphoric acid.

Dr. Carl Mohr formerly proposed a process for estimating phosphoric acid with uranium in presence of iron. He has now adopted a modification. In his original memoir he proposed to throw down the ferruginous solution of phosphate partially with uranium, and then to add so much potassium ferrocyanide as suffices for transforming the ferric phosphate. This transformation is often incomplete if but little iron oxide is present, as in animal charcoal and guano. It is therefore better to throw down the iron with potassium ferrocyanide before precipitating the phosphoric acid. Filtration is in either case unnecessary. Instead of precipitating the iron with pulverised potassium ferrocyanide, as directed in the author's first memoir, he prefers a 5 per cent. solution, which is introduced into a

small bulb-pipette drawn out below to a fine orifice. To regulate the outflow of the liquid a glass tap is adapted below the bulb.

When precipitating a ferruginous phosphatic solution it is needful to ascertain previously how many drops of the ferrocyanide solution are necessary. The solution is dropped in till a drop of the liquid gives a faint reddish or brown colouration. To a second portion there are added 1 or 2 drops fewer, and it is ascertained by a second test with uranium solution if the precipitation-point has been reached. It is necessary to count the drops exactly. In metallurgical or mining establishments where ores of the same class are always examined, a single estimation of the number of drops is sufficient to show how much ferrocyanide solution is always to be used for the precipitation of the iron.

D. Estimation of Phosphoric Acid by the Bismuth Process.—Take 2 grammes of the very finely pulverised phosphorite; put the weighed mineral into a flask, or glass beaker, and pour over it about 7 c.c. of nitric acid free from chlorine, and of 1.25 sp. gr. Heat the vessel and its contents for about $\frac{1}{2}$ hour nearly to the boiling-point, dilute with pure distilled water and filter; add to the well-washed filtrate as much water as will suffice to make up a quantity of 500 c.c. Take 100 c.c. of this liquid, representing 0.4 gramme of phosphorite; add another 100 c.c. of pure distilled water, heat to the boiling-point, and precipitate the hot fluid by the addition of a solution of bismuth nitrate prepared in the following manner:—

Take crystallised bismuth nitrate, dissolve in water; add as much nitric acid as is required to prevent precipitation on the addition of more water; make up the solution in such a manner as to obtain a litre of fluid containing 26 grammes of bismuth.

The precipitate, occasioned by the addition of the bismuth solution to the solution of phosphorite, is left standing till quite cold, and is then filtered off, the precipitate being washed with cold water. Next, the bismuth phosphate is dissolved, while on the filter, in a few drops of hydrochloric acid, and the solution is treated with ammonia and ammonium sulphide, and gently heated, until all the bismuth has been converted into sulphide. When this has been effected, the liquid is acidified with acetic acid, and heated to near the boiling-point; the precipitate is then collected on a filter, the last traces of sulphuretted hydrogen being eliminated by a few drops of chlorine water.

The phosphoric acid is estimated in the acetic acid solution by the uranium process.

A. Adriaanz gives the following modification of the bismuth process for estimating phosphoric acid in presence of iron and alumina:—To the hydrochloric solution of the substance in which the phosphoric acid is to be estimated, sodium thiosulphate is added first, so as to reduce the iron peroxide to protoxide; next, bismuth nitrate is added, and the vessel containing the substances heated for about four hours

on a water-bath. The precipitate which is formed is filtered off after twenty-four hours, and after having been well washed is dissolved in nitric acid. The hydrochloric and sulphuric acids present in this solution are next first eliminated by means of silver nitrate and barium nitrate, while the phosphoric acid is afterwards thrown down by means of bismuth nitrate. The bismuth phosphate precipitate is collected on a filter, washed, and lastly dissolved in hydrochloric acid, and estimated as magnesium ammonio-phosphate in the presence of ammonium citrate. This process may even be employed when the substance contains fifty times more alumina than phosphoric acid; but if the proportion of alumina be very large, it is best to add to the substance a weighed quantity of pure sodium phosphate. If the iron happens to be present in very large excess, it is necessary to redissolve the first bismuth precipitate and re-precipitate it a second time.

E. Estimation of Phosphoric Acid by the Lead Process.—For the estimation of phosphoric acid in coprolite or sombrerite, which contains a considerable amount of iron and aluminium, besides calcium, magnesium, &c., Mr. Warington considers that very few of the processes usually recommended for the estimation of phosphoric acid are here applicable. The molybdic acid method is inadmissible from the large amount of phosphoric acid to be estimated. The mercurial method fails owing to the presence of aluminium. The uranium method can be employed only if the iron be previously reduced by means of uranium protochloride. The tin method is free from all these objections, and is no doubt, when carefully conducted, an excellent process, but the time it takes up is considerable. The process which Mr. Warington prefers is given below.

The subject divides itself into two parts: the estimation of phosphoric acid and of the alkaline earths, and the estimation of iron and aluminium.

The nitric acid solution¹ of the mineral, previously freed from silica in the usual way, is treated cautiously with dilute ammonia to remove all unnecessary excess of acid; the clear liquid is then treated in one of two ways; either an excess of neutral lead acetate is added, or the solution is treated with lead nitrate, and digested with successive portions of finely-powdered litharge till slightly alkaline, the liquid in this case being finally acidified with a few drops of acetic acid. The former plan is generally to be preferred, though the precipitate is considerably more bulky, as only a portion of the iron, and probably none of the aluminium, is in this case precipitated with the phosphoric acid.

¹ When nitric acid alone is used to effect the solution of a coprolite a trace of phosphoric acid is sometimes left with the silica; it is therefore safest to dissolve in hydrochloric acid, and after evaporation to dryness to redissolve with nitric acid.

The precipitated lead phosphate is warmed for some minutes to induce aggregation, and then thoroughly washed by decantation, the washings being filtered. The washing water should be slightly warm, and contain a little ammonium acetate, otherwise the filtrate is apt to be turbid.

There are several ways of treating the precipitate. It may be dissolved in nitric acid (which for this purpose must not be too weak), the solution diluted and the lead precipitated by means of sulphuretted hydrogen; or the nitric solution may be treated with an excess of sulphuric acid and the lead precipitated as sulphate. The first plan is unexceptionable and yields excellent results; the necessary dilution entails, however, a subsequent concentration which occupies some time. If lead acetate has been used, the best plan for ordinary purposes is to treat the lead phosphate with oxalic acid and a few drops of potassium oxalate. The decomposition is rapid and complete; the lead oxalate may after a short time be separated by filtration. Oxalic acid does not perfectly decompose the densely aggregated precipitate obtained with lead nitrate and litharge. The action of sulphuric acid on the precipitate is incomplete, whether lead acetate or nitrate has been employed. Lead oxalate is nearly insoluble in oxalic acid; its solution, if treated with sulphuretted hydrogen water, appears only very slightly discoloured when looking through a depth of several inches.

The lead being separated, the solution now contains the whole of the phosphoric acid with a little iron; some citric acid is added and an excess of ammonia; the clear solution is finally treated with 'magnesia mixture,' and the phosphoric acid separated in the usual way.

The calcium, magnesium, and alkalis are readily estimated in the original filtrate from the lead phosphate, the excess of lead being first precipitated by means of sulphuretted hydrogen. A little citric acid must be added before the solution is made ammoniacal for the estimation of the magnesium, to hold in solution the iron and aluminium. This method has the advantage of speed, and admits of the convenient estimation of all the bases except iron and aluminium. It is applicable to the analysis of all the phosphates employed in agriculture.

F. Estimation of Phosphoric Acid by Means of Mercury.—The nitric acid solution of the phosphate is evaporated to dryness with excess of metallic mercury, the residue collected and washed, mixed when dry with sodium carbonate, and very gradually heated to fusion. The fused mass is dissolved in water, neutralised with acid, and the phosphoric acid estimated as magnesium ammonio-phosphate. This method gives very accurate results.

G. Estimation of Phosphoric Acid by Means of Iron.—Dissolve the phosphate in acid, add to the solution iron perchloride, and

on a water-bath. The precipitate which is formed is filtered off after twenty-four hours, and after having been well washed is dissolved in nitric acid. The hydrochloric and sulphuric acids present in this solution are next first eliminated by means of silver nitrate and barium nitrate, while the phosphoric acid is afterwards thrown down by means of bismuth nitrate. The bismuth phosphate precipitate is collected on a filter, washed, and lastly dissolved in hydrochloric acid, and estimated as magnesium ammonio-phosphate in the presence of ammonium citrate. This process may even be employed when the substance contains fifty times more alumina than phosphoric acid; but if the proportion of alumina be very large, it is best to add to the substance a weighed quantity of pure sodium phosphate. If the iron happens to be present in very large excess, it is necessary to redissolve the first bismuth precipitate and re-precipitate it a second time.

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then excess of sodium acetate. Boil for some time till the whole of the iron is precipitated. The whole of the phosphoric acid will come down with the iron.

If the substance under analysis is free from iron or aluminium, the iron perchloride should be added in known quantities from a standard solution. Upon now washing, drying, and weighing the precipitate, the excess of weight over that due to the iron sesquioxide present represents phosphoric acid.

If, however, iron or aluminium is present, the precipitate is dissolved in hydrochloric acid, citric acid is added, and the phosphoric acid precipitated by 'magnesia mixture.' Were it not for the inconvenience of working with so large a bulk of iron precipitate, this process would leave little to be desired.

H. Estimation of Phosphoric Acid by the Molybdic Acid Process.—To the nitric acid solution of the phosphate, add a large excess of solution of ammonium molybdate in nitric acid; a yellow precipitate of ammonium phosphomolybdate falls down, which is almost insoluble in acids. Allow the mixture to stand in a warm place for a day, filter, and wash with a dilute acid solution of ammonium molybdate. Dissolve the precipitate in ammonia, and to the clear solution add 'magnesia mixture.' This process is very accurate when small quantities of phosphoric acid have to be estimated in the presence of large quantities of iron or aluminium. No arsenic or silicic acid must be present, as it would precipitate with the molybdenum solution, and afterwards with the magnesia mixture. According to Nuntzinger's analysis of ammonium phosphomolybdate, after drying at 212° F., it contains 8.577 per cent. of ammonium oxide, 8.962 per cent. of phosphoric acid, and 92.461 per cent. of molybdic acid.

The following process has proved satisfactory in the experience of many years :—

From 25 to 50 c.c. of the solution of the phosphate, which may contain from 0.1 to 0.15 gramme phosphoric acid, are placed in a porcelain capsule with the addition of 100 to 150 c.c. molybdic solution. The mixture is heated on the water-bath, with occasional stirring, to about 80° , set aside for an hour, filtered through a plain filter, and the yellow precipitate (which need not be entirely rinsed on to the filter) is washed with dilute molybdic solution. The porcelain capsule is then placed under the funnel, the filter is pierced with a platinum wire, and the precipitate is washed into the capsule with dilute ammonia ($2\frac{1}{2}$ per cent.), washing the filter-paper well, dissolved, stirring with the glass rod, and the solution washed into a beaker with ammonia of the same strength, enough of which is added to make up a volume of 100 c.c. About 15 c.c. of magnesium chloride mixture are then gradually dropped in, constantly stirring. After the mixture has been set aside for two hours, covered with a glass plate, it is filtered through a plain filter, the weight of the ash being known,

and the precipitate is washed with dilute ammonia of the same strength till a portion of the filtrate, after being acidulated with nitric acid, does not show the presence of chlorine with silver nitrate. The dried precipitate is separated from the filter, placed in a porcelain crucible; the paper is charred but not incinerated, and the char placed in the crucible, which is heated first gently, then ignited strongly for ten minutes in a slanting position over a Bunsen burner, and finally exposed for five minutes to a blast-flame, let cool in the desiccator, dried, and weighed.

The first 6 or 8 c.c. of the magnesia mixture should be added very cautiously.

The final ignition before the blast serves to volatilise any traces of molybdic acid which may have been precipitated.

The molybdic process is used under the following conditions at the Halle Agricultural Station:—A quantity of the sample is taken containing from 0.1 to 0.2 gramme phosphoric acid. The bulk of the solution should be from 50 to 100 c.c. The molybdic solution is prepared by dissolving 150 grammes ammonium molybdate in 1 litre water, and pouring this into 1 litre of pure nitric acid. The quantity of the solution used should be such that for 1 part of phosphoric acid present there should be 50 parts of molybdic acid. Hence about 100 c.c. of the above solution are necessary for 0.1 gramme of phosphoric acid. A large excess of molybdic acid is not to be desired, since a certain quantity of free molybdic acid is almost always deposited, and does not readily redissolve in ammonia. For the complete precipitation of the phosphoric acid it is sufficient to let the mixture digest from 4 to 6 hours at 50° C. After cooling, the yellow precipitate is filtered, and washed with a mixture of the molybdic solution and water, equal parts. The yellow precipitate is dissolved on the filter with *hot* ammonia, 1 part of commercial ammonia to 8 parts of water. As little as possible is used, and the excess is neutralised with hydrochloric acid, which is added as long as the precipitate formed redissolves quickly. The liquid must then be cooled before adding the magnesia mixture, as, if it is hot, basic magnesium salts are sometimes thrown down. The magnesia mixture is made up with 110 grammes crystalline magnesium chloride, 140 ammonium chloride, 700 liquid ammonia, and 1,800 water. To precipitate 0.1 gramme of phosphoric acid we require 10 c.c. of this mixture. After adding the magnesia mixture, we pour in $\frac{1}{3}$ of its volume of concentrated liquid ammonia. The total bulk of the liquid should not exceed 100 to 110 c.c. In 3 or 4 hours the precipitate is ready for filtration.

The precipitate is washed on the filter with dilute ammonia (8 : 1) until chlorine can no longer be detected in the filtrate. No subsequent correction is needful. When dry, the precipitate is removed from the filter (which is burnt separately). The flame must be feeble

at first, and be gradually increased. It is finally ignited with the gas blowpipe.

R. Finkener finds that hydrochloric and nitric acid hinder or delay the formation of the yellow precipitate, whilst dissolved molybdic acid promotes or accelerates it. Hydrochloric acid in the solution acts more powerfully than nitric, and ammonium nitrate more powerfully than ammonium chloride. The author's solution contains per litre 88 grammes molybdic acid, 141 grammes nitric acid, and 19.4 grammes ammonia. When precipitating phosphoric acid the quantity of free nitric acid must always be more than enough to prevent the formation of a precipitate in the absence of phosphoric acid, but a considerable quantity of ammonium nitrate may be dissolved in the liquid. In ordinary cases the phosphoric acid will be totally precipitated in less than twelve hours, if so much molybdic mixture is added as to make up four times the volume of the phosphoric solution, and if in every 100 c.c. of the mixture there are dissolved 25 grammes ammonium nitrate. For washing the precipitate is employed a strong solution (20 per cent.) of ammonium nitrate, to which at first $\frac{1}{30}$ of its volume of nitric acid is added. The washing is completed when the washings are no longer coloured by potassium ferrocyanide. The precipitate may be brought into a condition fit for weighing by the following operations:—After removing most of the ammonium nitrate by means of water the contents of the filter are washed into a weighed porcelain crucible. Anything adhering to the paper is dissolved in a little warm dilute ammonia, the solution is concentrated by evaporation, nitric acid is added in excess, the whole is quickly poured into the porcelain crucible, the liquid is expelled by evaporation, and the ammonium nitrate driven off by a flame moderated by wire gauze. The residue is hygroscopic, and must be cooled over sulphuric acid, and quickly weighed in the covered crucible.

Concerning the preparation and use of the molybdic liquid, Champion and Pellet dissolve 10 grammes of molybdic acid in 15 c.c. of ammonia diluted with 8 c.c. of water, and then pour this clear solution drop by drop, and stirring continually, into 50 c.c. nitric acid diluted with 80 c.c. of water, and let the mixture stand for some days at 40° to 45°; so that it may deposit any silica or phosphoric acid present. The clear liquid is then preserved in a well-stoppered bottle. By still further increasing the quantity of water, adding 80 c.c. to the ammonia, and 50 c.c. to the nitric acid, a very sensitive reagent is obtained, which does not deposit any sediment in the course of two months. It is unnecessary to add any acid, especially tartaric acid, to the solution of ammonium molybdate if it is free from phosphoric, arsenic, or silicic acid.

Among the methods of using the reagent, the following is the simplest:—The sample is dissolved in an excess of nitric and hydrochloric acid; there is poured into it a solution of ammonium

molybdate (without nitric acid), the mixture is boiled and left to settle. In this manner the process is much simplified, as it is merely necessary to dissolve *pure* ammonium molybdate in water when required. The nitric or hydrochloric acid must contain no lead, silver, tin, or antimony, and no organic matter must be present, especially tartaric acid.

Recovery of Molybdic Acid from the above Operation.—The acid liquors, the filtrates from the yellow precipitate, are mixed with the ammoniacal wash-waters from the magnesium ammonio-phosphate precipitates, and, in addition, there is added sodium phosphate solution, in the proportion of 1 part of phosphoric acid to 80 of molybdic acid; after which, the fluid is left at rest for 24 hours in a warm place. The precipitate is collected on a filter and washed, until the filtrate begins to run slightly turbid: the precipitate is next dried in a water-bath, then dissolved in ammonia, and the solution poured into nitric acid in which 2 or 3 parts of pure magnesia have been dissolved. The ensuing precipitate of magnesium ammonio-phosphate is next removed; and, after having been standing for some time, in order to give time for a small quantity of molybdenum phosphate to settle, the solution is fit for use again as ammonium molybdate.

Drs. Stunkel and Wetzke and Prof. Wagner have examined the conditions upon which the accuracy of the molybdic method depends, and give the following as the best means of carrying out this process:—From 20 to 25 c.c. of a solution of phosphate free from silica, and containing 0.1 to 0.2 gramme of phosphoric acid, are placed in a beaker, and mixed with so much solution of ammonium nitrate (see below), and so much molybdic solution, that the total liquid may contain 15 per cent. ammonium nitrate, and not less than 50 c.c. of molybdic solution per 0.1 gramme phosphoric acid. The contents of the beaker are heated to 80° or 90° in the water-bath, set aside for an hour, filtered, and the precipitate washed with dilute ammonium nitrate. The beaker is now set under the funnel, the filter pierced with a platinum wire, the precipitate rinsed into the beaker with ammonia at 2½ per cent., washing the filter-paper well. It is then dissolved, stirring with a glass rod, and ultimately so much of the weak ammonia added as to make up the volume of the liquid to about 75 c.c. To 0.1 gramme phosphoric acid 10 c.c. magnesia mixture are dropped in, stirring continually; the beaker is covered with a glass plate, and set aside for 2 hours. The precipitate is then filtered off, washed with ammonia at 2 per cent., and dried. The precipitate is introduced into a platinum crucible, putting in also the rolled-up filter; the crucible is covered and heated till the filter is carbonised. It is then placed in a slanting position in the flame of a Bunsen burner for 10 minutes, and is afterwards ignited before the blast for 5 minutes, let cool in the desiccator, and weighed.

The strength of the solutions to be employed is as follows:—

1. *Molybdic Solution.*—150 grammes ammonium molybdate are

dissolved with water, so as to make 1 litre, and poured in 1 litre nitric acid of specific gravity 1.2.

2. *Concentrated Solution Ammonium Nitrate*.—750 grammes ammonium nitrate dissolved with water to the bulk of 1 litre.

3. *Dilute Solution Ammonium Nitrate*.—100 grammes ammonium nitrate dissolved in water to the bulk of 1 litre.

4. *Magnesia Mixture*.—55 grammes crystallised magnesium chloride and 70 grammes ammonium chloride are dissolved in 1 litre ammonia at $2\frac{1}{2}$ per cent.

The process differs in three points from that commonly followed:—

1. The precipitation and washing of the molybdic precipitate is executed in presence of ammonium nitrate, for the practical purpose of economising time and materials.

2. The authors rinse the precipitate from the perforated filter with ammonia at $2\frac{1}{2}$ per cent., and add the magnesia mixture at once, whilst generally the precipitate is dissolved on the filter with heated concentrated ammonia, the ammoniacal liquid is neutralised with hydrochloric acid; the liquid, which is thus heated, is allowed to cool, then mixed with magnesia mixture, and finally diluted by $\frac{1}{3}$ with ammonia. This modification of the common process is recommended for practical reasons.

3. The magnesia mixture is added drop by drop, and with continual stirring, whilst other instructions are silent on this head. These precautions are given because otherwise an impure precipitate and an excess of phosphoric acid are obtained.

As regards the first point, E. Richters demonstrated ten years ago that the separation of the molybdic precipitate, which is interfered with by the presence of much acid and certain salts, *e.g.* potassium and sodium sulphates, is greatly facilitated by the addition of ammonium nitrate. This recommendation is also given by Gilbert. The authors have found, in a special series of experiments, that a much smaller excess of molybdic solution suffices if ammonium nitrate is present.

They have also found experimentally that the application of a heat of 80° and a rest of 1 hour will suffice to effect the precipitation of all the phosphoric acid. If the temperature exceeds 90° , free molybdic acid separates out, which does not readily dissolve in ammonia, and is therefore troublesome.

The molybdic precipitate is insoluble both in dilute molybdic solution and in a 15 per cent. solution of ammonium nitrate slightly acidulated with nitric acid. Hence this mixture may be safely used for washing the precipitate, even without the addition of molybdic solution. But the authors find, further, that a 10 per cent. solution of ammonium nitrate gives satisfactory results, even without acidulation with nitric acid, and this accordingly they recommend.

The reason for the direct addition of magnesia mixture to the ammoniacal solution of the molybdic precipitate is as follows:—The

simple rinsing the precipitate from the filter, and washing the paper with dilute ammonia, is much more easily and readily effected than dissolving the precipitate upon the filter with hot ammonia followed up in the ordinary manner, by which, further, too much ammonium chloride is often formed.

As regards the third point the authors have previously pointed out that a sudden addition of magnesia mixture occasions an impure precipitate. A pure precipitate and an accurate result can be obtained only by a very gradual addition of the magnesia mixture with constant stirring.

There remain only three questions:—

1. In how far is the degree of concentration of the solution of influence in precipitation with magnesia mixture? The experimental reply is that it may safely vary within wide limits.

2. How long must the solution be let stand, after the addition of the magnesia mixture, before it can be filtered? The results of the authors, in accord with those of Abesser, Jani, and Märcker, show that it is not merely unnecessary to allow the mixture to stand 12 to 24 hours, as was formerly customary, but, on the average, more accurate results are obtained (supposing a quantity of phosphoric acid exceeding 0.1 milligramme) by filtering after about 2 hours.

3. In how far is the concentration of the ammonia used for washing of the magnesia precipitate of importance? The authors conclude that the solubility of the magnesia precipitate is so exceedingly small that there is no need to cut short the washing, as is almost always recommended.

R. Finkener proposes the following method for the direct estimation of phosphoric acid from the weight of the phospho-molybdic precipitate. The following conditions must be observed in precipitation:—The solution must contain a sufficiency of free nitric acid. The molybdic solution added must be fourfold the volume of the phosphoric solution to be precipitated, and at least $\frac{1}{3}$ of the molybdic acid added must be in excess of the quantity required for combination with the phosphoric acid. In every 100 c.c. of the volume of liquid after the addition of the molybdic solution must be dissolved 25 grammes ammonium nitrate. The precipitate of ammonium molybdate is filtered after standing for 12 hours, and is washed with a 20 per cent. solution of ammonium nitrate, to which at the beginning of the washing $\frac{1}{30}$ of its bulk of nitric acid is added. After removal of the greater part of the ammonium nitrate by means of water the contents of the filter are rinsed into a porcelain crucible, the matter adhering to the paper is dissolved in hot dilute ammonia, the solution is concentrated by evaporation, an excess of nitric acid is added, the solution is poured into the porcelain crucible, the liquid is evaporated away, and the ammonium nitrate expelled by gently heating over a flame placed below a wire gauze. The volatilisation of the ammonium nitrate is found to

be complete when a cold watch-glass placed over the crucible is not clouded. The ammonium phospho-molybdate is not decomposed if a needlessly high temperature is avoided. The residue is hygroscopic, and must be cooled in the desiccator over sulphuric acid, and quickly weighed in a covered crucible. The residue is said to contain 8.794 per cent. phosphoric acid.

A. Attarberg has determined the conditions in which the most rapid and complete separation of the ammonium phospho-molybdate can be effected. He finds that by boiling the solution with molybdic acid solution the phosphoric acid is precipitated in a satisfactory manner. The boiling is effected in a beaker of moderate size, stirring continually to prevent bumping. The heat is obtained from a naked lamp flame beneath a wire gauze. The precipitate settles very quickly, and can be at once submitted to further treatment.

I. Estimation of Phosphoric Acid by Means of Oxalic Acid.—Dissolve the phosphorite in acid, and separate the silica in the usual way. Add dilute ammonia carefully until a slight permanent opalescence is produced, but be careful not to neutralise. Add just sufficient dilute oxalic acid to remove this opalescence, and allow it to stand. The solution will become yellow if iron is present. Now precipitate the calcium by an excess of ammonium oxalate, warm, and filter. Evaporate the filtrate, add citric acid to hold the iron and aluminium in solution, then add ammonia in excess and 'magnesia mixture' to precipitate the phosphoric acid. The calcium oxalate cannot be used to estimate the amount of calcium present, for there will be a slight deficiency owing to its solubility in oxalic acid.

The magnesium ammonio-phosphate always contains a trace of calcium oxalate, insufficient, however, to vitiate the results for ordinary purposes. When great accuracy is required the best plan is to redissolve the precipitate in dilute acetic acid, filter from calcium oxalate, and then re-precipitate and weigh as usual.

Dr. B. W. Gerland thus modifies the oxalic acid process:—The properly prepared solution of the weighed sample in hydrochloric or nitric acid is neutralised as much as possible without forming a permanent precipitate, heated to boiling, and oxalate added in small excess. If the dilution is already sufficient ammonium oxalate may be added in crystals. Sodium (or ammonium) acetate is added in sufficient quantity to take up the free mineral acid, and the liquor is removed from the fire. The calcium oxalate settles rapidly as a heavy granular powder. The liquor, which appears clear whilst hot, becomes turbid on cooling, but after 2 hours' rest is again clear. The filtration of the calcium oxalate can now be proceeded with; it requires very little time. The precipitate is free from iron and aluminium phosphates, which is readily proved by dissolving the calcined residuum in hydrochloric acid and adding ammonia, when no precipitate will be formed.

From the filtrate and wash-waters of the calcium oxalate iron and aluminium are to be separated. Ammonia alone does not effect it completely, boiling assists it, and the addition of bromine-water still more; but, to make the separation complete, it is advisable to add ammonium sulphide, and allow the sample to stand in a warm place until the liquor has cleared itself, and assumed a bright yellow colour. It is then filtered with the known precautions. The precipitate is generally free from magnesia, particularly if ammonia was not added in too great excess, but contains, besides aluminium phosphate and iron sulphide, a not insignificant quantity of silica, even if the solution has been previously evaporated to dryness. Phosphoric acid retains silica with a tenacity similar to the vanadic acid. For the analysis of the iron and aluminium precipitate the molybdic acid method is the most convenient. Instead of using ammonium sulphide, the liquor may be treated with chlorine, or evaporated with sodium carbonate, and the residuum calcined for the destruction of the oxalic acid. The filtrate from the ammonium sulphide precipitate is to be concentrated, and the magnesia precipitated with part of the phosphoric acid by ammonia. Lastly, the remaining phosphoric acid is separated by magnesia mixture.

With these modifications the 'oxalic method' compares favourably in point of convenience with Sonnenschein's, and yields results no less accurate.

K. Estimation of Phosphoric Acid as Calcium Phosphate.—This is a very common method of approximately estimating the value of guano, and sometimes bone-ash. The results are never very exact, but the method is simple and speedy, and will frequently give all the information that is required. The phosphate is dissolved in acid, and to the clear solution ammonia in very slight excess is added; the precipitated calcium phosphate is collected and weighed. With guanos which contain calcium phosphate and alkaline salts the results are tolerably accurate, but in the case of bone-ash the precipitated calcium phosphate contains lime mechanically carried down. The results are quite unreliable in the case of coprolites, although this method is sometimes used in their valuation.

L. Estimation of Phosphoric Acid by Volatilisation.—The author has not experimentally verified this process, but as the principle is novel, and appears likely to be of use in some cases, it may not be out of place to insert an abstract of it along with other processes. The author is Dr. Th. Schloesing.

By heating to whiteness a mixture of carbon, silica, and calcium, magnesium, or aluminium phosphate, the whole of the phosphorus is not extracted, owing to the unavoidable imperfection in the mixture. To avoid this drawback the carbon is replaced by a current of reducing gas, and the silica and phosphate are intimately mixed by dissolving the latter in very little nitric acid, and by adding silica to the hot

liquid until it refuses to absorb more. By drying on a sand-bath, and heating to redness, a mixture is obtained which does not adhere to platinum, and which can be transferred when necessary with no loss whatever.

As phosphorus attacks platinum, and as it is necessary to preserve the silicate in its integrity, which could not consequently be placed in contact with porcelain, the mixture of phosphate and silica is transferred to a charcoal boat, to introduce it afterwards into a tube of Bayeux porcelain. This kind of boat is made by pouring a paste of carbonised sugar and syrup through a tube made of blotting-paper; after a few minutes remove the excess affixed to the paper; next dry, and then make red hot; then cut the tube into two half-cylinders, and close the ends with a paste more solid than the first. The tube may be heated in various ways, but gas is the best, as then it is not necessary to preserve the tube from contact with the combustible, and the same tube serves for several operations. Four strong blowpipes should be arranged vertically, at equal distances, within a space of 8 centimetres, and projecting their flames on the porcelain tube, whose heated part, about 16 centimetres, is surrounded by platinum foil, and placed in a muffle composed simply of a few refractory bricks. In 7 or 8 minutes the tube reaches white heat.

The most suitable reducing gas is carbonic oxide, which is a sufficient reducer even for phosphoric acid; it must be dry, as phosphorus decomposes water at red heat, and should retain little carbonic acid, which might interfere with its reducing power.

In two experiments made by Dr. Schloesing, a mixture of magnesium and silica phosphate, containing 0.062 gramme of phosphoric acid, lost 0.063; and a mixture of aluminium and calcium phosphates with silica, containing 0.124 gramme of phosphoric acid, lost 0.123 gramme. The silica produced was agglomerated in the form of a porous scoria.

In these two experiments the heating lasted half an hour, and each consumed one and a half litres of carbonic oxide.

When phosphates are free from aluminium, the silicates produced abandon their bases to hot nitric acid, although they contain some excess of silica and have undergone a high temperature. When phosphates contain aluminium the silicates are again destroyed by digestion with potash at 150° to 200° C.; thus, in both cases, the bases can be easily estimated after the removal of the phosphoric acid.

When the phosphorus has been set at liberty, it may be collected and estimated directly. The porcelain tube may be luted on to a thin silver tube containing metallic copper, and heated to dull redness. The silver will not be attacked, but the copper will absorb the whole of the phosphorus, the quantity of which will be indicated by the increase of weight of the silver tube. But we do not in this way get a compound so well defined as might be desired; hence the author pre-

fers transforming the phosphorus into a phosphate which should realise this condition. The gaseous current from the porcelain tube is passed through a bulb tube containing a solution of silver nitrate. The whole of the phosphorus condenses in it, forming black silver phosphide, and some phosphate dissolved by the displaced nitric acid. The bulb tube should be heated in a water-bath to 80° or 90° C., for the true combination of carbonic oxide and phosphorus mentioned by Berzelius only abandons all its phosphorus with the aid of heat. The silver liquid is decanted into a platinum capsule and evaporated; on the residue pour hot nitric acid with which the bulbs have been washed; all the phosphorus is thus converted into phosphate; evaporate to dryness, heat till the excess of silver nitrate is fused and no perceptible acid vapours are disengaged. Under these conditions the phosphoric acid unites with exactly three equivalents of silver, constituting the tribasic phosphate. The resulting salt is washed by simple decantation, then dried and weighed.

Silver phosphate possesses two advantages in analytical processes; its equivalent is very high, and its composition is rapidly verified by the estimation of the silver. A little phosphorus is condensed in the porcelain tube, but it is red phosphorus, emitting no vapour when cold, and it may be recovered without loss by rinsing out the tube with silver nitrate and then with nitric acid; these washings are added to the contents of the bulbs.

The production of tribasic silver phosphate in presence of fused silver nitrate is not limited to the instance just given; ammonium, potassium, and sodium phosphates behave like pure phosphoric acid. This, then, is a very sure method of estimating phosphoric acid by silver phosphate, either when alone or accompanied by an alkali, but in the absence of any earthy or metallic base.

M. Estimation of Phosphoric Acid Volumetrically.—No volumetric process for estimating phosphoric acid is sufficiently good for very accurate work, but owing to the ease with which these estimations are made and the great advantage of their rapidity when many estimations are to be made every day, it is generally felt that in commercial analyses it is allowable to sacrifice a certain amount of accuracy for the sake of speed, provided always that the errors of experiment are not sufficiently great to be of commercial consequence. Mr. Burnard has been in the habit of employing a modification of the well-known uranium volumetric process in the analysis of phosphatic manures, and in the following description he has drawn attention to several precautions which are necessary to ensure the requisite degree of accuracy, for often, with the greatest care as to uniformity of volume in samples tested, it is frequently doubtful when the point of colouration is obtained. In two estimations of the same sample made side by side it is seldom that complete uniformity of results are obtained. Much depends on the size of the drop falling into the little

pool of ferrocyanide, something in the manner in which the drop falls; while in all cases *time* is an essential element in the question. If testing be continued until the brown colouration is evident, the result will be far too high. To prove this, let the operator, in reaching the desired indication, cover over his slab (to prevent drying) and leave it so some hours, say until next morning, when he will find the point to be 5 or 6 units below that indicated over-night. But even now there is much uncertainty, for if he has (as he should always have) tried two side by side, he will frequently be perplexed in making his decision. By adopting the following method all doubt is dissipated, and much greater accuracy obtained.

If the composition of the substance be quite unknown, a preliminary examination is made, which soon shows the probable range of its percentage of phosphoric acid. But in general this is unnecessary. A plain porcelain slab is used, pits or indentations for the pools being objectionable, as hindering due access of light to the body of the pool. To prevent flowing about, a ring of cork, giving a clear space of $\frac{1}{2}$ of an inch, pressed on some hard tallow and then on the slab, leaves a faint but effectual wall of grease.

The method may be best explained as follows, giving an actual estimation by way of illustration. Three portions of the same solution, being each 100 septems, were taken and dried side by side on the same slab.

No. 1.—26	28	30	32	34	septems. ¹
No. 2.—25	27	29	31	33	"
No. 3.—24	25	26	27	28	"

Now, at the conclusion of the actual testing, not one exhibited the slightest trace of brown colouration; they all appeared precisely alike. They were then covered over and left until the morning, when one only, viz., 84, showed the red-brown colour, and that as an intensely bright eye in the centre of the pool.

Now, following out the modification here proposed, the slab was carefully put on a levelled stand before a fire, and the spots dried by radiant heat falling on their surfaces; gently drying in this way being preferable to any other, for rising from below the heat disturbs the settlement of the precipitate. When dry, and the slab just warm, water was carefully dropped on each spot, so as to dissolve the dried-up ferrocyanide, when, although on the dried slab there was not a trace of brown visible, the truth was revealed, and the reading became—

No. 1.—30 stood as the number.
No. 2.—29 " "
No. 3.—29 " "

¹ In the above each number is intended to represent a thin pool of potassium ferrocyanide, of about $\frac{1}{2}$ inch diameter; and also in each case the number of septems of uranium nitrate employed.

At the time of testing there was no exhibition of colour; next morning 84 stood revealed; but on drying and redissolving, as explained, 29 was unquestionably the number. It is obvious that, while a precipitate may be so slight as to render the colouration of a small pool difficult, yet by its settling down on the white slab it is immediately revealed on dissolving away the crust covering it.

M. Abesser, of Halle, effects the volumetric estimation of phosphoric acid as follows:—20 grammes of the sample are treated with water in a mortar. The lumps are broken up without pressing them strongly, and the whole poured into a litre-flask, which is filled with water up to the mark, closed with a stopper, shaken briskly for some minutes, and filtered immediately. This method of extraction is not applicable to superphosphates prepared from Lahn phosphorite, which must be extracted by washing on the filter.

The filtrate is examined with sodium acetate to find if there is a precipitate of iron phosphate. If there is a precipitate, 200 c.c. of the filtrate are mixed with 50 c.c. of a solution containing per litre 100 grammes of crystalline sodium acetate, and 100 grammes of concentrated acetic acid, equivalent to 80 or 40 grammes of glacial acetic acid.

Filter to separate the precipitate, wash on the filter three or four times in boiling water, ignite in a platinum crucible, and calculate 0.47 of the final weight as phosphoric acid.

The liquid filtered from the precipitate of iron phosphate is then titrated; 50 c.c. of this represent 40 c.c. of the original solution. If there is no precipitate of iron phosphate, titrate 50 c.c. with uranium solution, after the addition of 10 c.c. of a mixture of sodium acetate and acetic acid. The sodium acetate and free acetic acid are not without influence upon the appearance of the final reaction of uranium with potassium ferrocyanide. It is therefore necessary, in titrating the uranium solution with calcium phosphate, to add the above mixture in a quantity exactly equal to that used for superphosphates.

Titration of the Uranic Solution.—Five hundred grammes of uranium nitrate or acetate (crystalline), diluted with water to the bulk of 14 litres, yield a solution, of which 1 c.c. precipitates about 5 milligrammes of phosphoric acid. Nevertheless, it is prudent to take an excess of 25 to 80 grammes of the uranic salt, since there remains almost invariably a deposit of insoluble basic salts. As the nitrate always contains free nitric acid, we add, to neutralise it, sodium acetate in the proportion of 50 grammes to 500 grammes of the uranic salt. To the acetate we add, per 500 grammes, 50 to 100 grammes of concentrated acetic acid, which renders the solution of the salt more stable. It is needful to let the uranic solution stand some days before filtering, since the deposition of the basic salt does not take place immediately.

It is best to standardise, not with sodium phosphate, but with

an acid calcium phosphate, thus reproducing, as far as possible, the circumstances to be dealt with in the analysis of superphosphates.

To prepare the liquid for titrating the uranic salt, digest 5.5 grammes of tribasic calcium phosphate with dilute sulphuric acid.

The authors employ for this purpose the dilute sulphuric acid serving for the estimation of nitrogen by Will and Varrentrapp's method. After digestion, the mass is taken up with water and diluted to 1 litre. It is then filtered to remove calcium sulphate and the small quantity of basic calcium phosphate which has not been dissolved. It is more convenient, and quite as exact, to dissolve the pure basic calcium phosphate in a slight excess of nitric acid, and to estimate the amount of phosphoric acid contained in the liquid by adding ammonia and igniting the precipitate. It must not be forgotten that tribasic calcium phosphate, though it appears dry, still contains 10 to 15 per cent. of moisture, account of which must be taken in preparing the solution for standardising. Fifty c.c. of this liquid contain about 0.125 gramme of phosphoric acid, and are precipitated by 25 c.c. of the uranic solution prepared as above directed. For the titration itself take 50 c.c. of the solution, *i.e.* as much phosphoric acid as there is in the solution of a superphosphate at $12\frac{1}{2}$ per cent. (of which 20 grammes for 1 litre of solution); add 10 c.c. of sodium acetate, and run the uranic liquid into the cold solution till the reaction begins to appear. Then boil, and try the reaction of potassium ferrocyanide with a drop of the liquid upon a porcelain plate. To have the final reaction very distinct, dry pulverised potassium ferrocyanide must be used. A quite freshly prepared solution also gives a distinct and regular reaction, but an old one does not.

The solution of superphosphate is estimated in the manner just described, in 50 c.c. With very rich superphosphates the final reaction loses somewhat of its distinctness from the uranium phosphate, which is abundantly precipitated. To avoid this inconvenience, take 25 c.c. in place of 50, and dilute with an equal volume of water.

For the estimation of phosphoric acid in Baker guano and similar materials, Dr. Gilbert recommends the following procedure:—2.5 grammes of the sample, dried if the manure is in a very moist condition, are mixed with 4 times its weight of a finely powdered mixture of 2 parts of dry sodium carbonate and 1 part of potassium chlorate, which should be kept ready. The mixing is performed with a glass rod fused round at the end, in a capacious platinum crucible. The dust adhering to the rod is wiped off with a bit of Swedish filter-paper, and added to the mixture in the crucible. The flame applied is small, and is not brought very near, and under these conditions the ignition proceeds quietly without loss. As soon as the contents of the crucible are white the heat is increased, and the material is kept in flux for a quarter of an hour at full redness. When cold the crucible is placed

in a beaker covered with about 150 c.c. of water, covered with a watch-glass, and about 80 c.c. of nitric acid, of sp. gr. 1.25, are poured down the side into the beaker. The mass dissolves, if no clay or sand is present, easily and regularly. If silicic acid is present, it is removed in the usual manner. The solution is then made up to 500 c.c., and used for the estimation of phosphoric acid. The uranium volumetric method he modifies as follows:—100 c.c. are put in a beaker for a preliminary trial. The liquid is rendered faintly alkaline with pure soda-lye, and then made acid again with a little acetic acid. This procedure is preferable to adding sodium acetate. The solution can be at once titrated, as the raw materials in question rarely leave a distinct precipitate of iron or aluminium phosphate undissolved.

Solution of uranium acetate is then allowed to drop into the *cold* solution. The solution of potassium ferrocyanide is to be prepared fresh daily, or the dry salt applied in powder. In gravimetric estimations of phosphoric acid the author recommends that the magnesia mixture be made without sulphate, which, if present, is partially deposited along with the double phosphate. The proportions are:—For 1 litre, 101.5 grammes crystalline magnesium chloride, 200 grammes ammonium chloride, and 400 grammes ammonia of sp. gr. 0.96. In the analysis of materials like ground bones, animal charcoal, and gelatinous bodies, the potassium chlorate in the fusion mixture is replaced with saltpetre. The Baker guano contains 45.98 per cent. of phosphoric acid; the Jarvis 86.71 per cent.; the Enderberry, 44.11 per cent.; and the Starbuck, 85.54 per cent.

S. W. Johnson and E. H. Jenkins propose the following volumetric method for the estimation of phosphoric acid in manures:—The standard acid used in other volumetric work answers perfectly for this. A strong, nearly saturated, solution of ammonium tartrate, free from carbonic acid, and a solution of some magnesium salt, are also necessary. The latter is prepared by dissolving 70 grammes of magnesium sulphate and 195 grammes ammonium chloride in 1 litre of water. 10 c.c. of this solution contain twice the amount of magnesium necessary to precipitate 0.1 gramme phosphoric acid (P_2O_5). A suitable amount of the phosphate (in most cases 1 gramme is a convenient quantity) is dissolved in hydrochloric acid, the solution nearly neutralised with ammonia, and ammonium tartrate solution is added, 10 c.c. at a time, till the solution remains perfectly clear when slightly alkaline. Add a suitable quantity of the magnesium mixture, and either stir vigorously with a rod, or, if the precipitation is made in an assay-flask, as it can be very conveniently, shake occasionally. When the precipitation is nearly complete add enough ammonia to make it very strongly alkaline, and let it stand six to twelve hours. It can then be filtered, preferably on the pump, and washed with equal parts of strong alcohol, 85 to 90 per cent., and water. No pains are taken to detach the precipitate from the glass. When the dish and precipitate

are washed until the washings no longer react alkaline, the filter and precipitate are brought back into the beaker or flask, a *little* water and a few drops of cochineal tincture are added, and it is titrated. This is best done by adding an excess of standard acid at once, stirring so that all the precipitate shall be wetted with it, and after it has stood a few minutes, titrating back with standard alkali.

This process requires less than half the time and labour necessary for the molybdic method, is scarcely less accurate, and appears to be generally applicable.

It has been shown that while ammonio-magnesium phosphate is totally insoluble in a large excess of ammonium tartrate, it is soluble in excess of ammonium citrate, and hence all methods based on the use of citric acid are faulty. It is a fact also that ammonio-magnesium phosphate is largely soluble in ferric and aluminic solutions containing *insufficient* ammonium tartrate.

It is therefore necessary in presence of iron to add ammonium tartrate more than enough to produce a reddish-yellow solution—enough, in fact, to make a greenish-yellow solution, as Otto has indicated. A similar excess of ammonium tartrate is also requisite in presence of aluminium, and while there is no colour-indication of the suitable quantity, a large excess does not appear to retain ammonio-magnesium phosphate in solution, unless the liquids are too concentrated.

Volumetric Estimation of Phosphoric Acid in Presence of Ferric Oxide.—Dr. C. Mohr proposes the following process:—2 to 5 grammes of the finely-powdered mineral are repeatedly boiled with small quantities of dilute nitric acid; the liquids are mixed in a measuring flask containing 100 or 250 c.c., and when cold filled up to the mark. In case of superphosphate similar proportions are observed, but distilled water is used instead of nitric acid. 10 or 25 c.c. of the filtrate are mixed with a solution of sodium acetate till a permanent turbidity is produced. The solution of uranium acetate is then allowed to flow in, heating gently at first, and afterwards to a boil, and before the precipitation is at an end a few granules of potassium ferrocyanide are added. The ferric phosphate is decomposed, the phosphoric acid enters into solution, the ferric oxide becomes Prussian blue and mixes with the uranium phosphate. The complete transformation of the ferric oxide into Prussian blue is ascertained when a drop of the clear liquid upon a porcelain plate shows no further colouration with ferrocyanide. The hot liquid very rapidly deposits the suspended precipitate. The author presses the rounded end of a moist thin glass rod upon ferrocyanide in a dry powder, when so much clings to the glass as to be sufficient for 10 c.c. of a mineral containing a slight amount of iron. It is important to defer the further addition of the uranium solution till all the ferric oxide is transformed. The addition of the uranium solution is then continued till the known colouration with

potassium ferrocyanide indicates the end of the process. The first drop of uranium solution should not occasion a red colouration where it falls. If this happens, a new portion must be taken, and the operation repeated. As in the ordinary process of titrating phosphoric acid with uranium, the solution is rarely absolutely free from iron, the final reaction disappears after it has been already produced—a circumstance which often leaves the analyst in doubt to the extent of an entire c.c. This disappearance of the final reaction may be avoided by the careful application of the method described above.

Mr. E. Perrot bases a process on the precipitability of calcium phosphates by ammonia; the solubility of calcium and magnesium phosphates in acetic acid, and the insolubility of iron and aluminium phosphates in this reagent; and on the power of the soluble phosphates, acid or basic, to precipitate silver salts as a yellow tribasic silver phosphate, insoluble except in ammonia. He dissolves 6.895 grammes pure silver nitrate in distilled water, and makes up to 1,000 c.c.; this corresponds to 4.565 grammes metallic silver per litre; 100 c.c. of this solution precipitate 0.71 gramme phosphoric acid. He dissolves 5.414 grammes sodium chloride in distilled water, and makes up to 2,000 c.c.; 100 c.c. of this solution precipitate 0.5 of silver. He dissolves the phosphatic matter in nitric acid of sp. gr. 1.08. The solution is filtered and the insoluble part washed with hot distilled water; the washings are added to the acid liquid, which is supersaturated with ammonia. The precipitate is washed with ammonia water upon a small filter, and it is then dissolved upon the filter (changing the recipient) by sprinkling it with acetic acid. The calcium and magnesium phosphates alone are dissolved. The liquid is mixed with ammonia till a precipitate begins to appear, which no longer dissolves on shaking. This precipitate is made to appear by the addition of a drop of acetic acid. This liquid should be collected in a stoppered bottle, holding 250 c.c. There are then added by means of a graduated pipette, 100 c.c. of the standard silver solution. On agitation the characteristic yellow precipitate of silver phosphate appears. When it has settled, the excess of silver remaining in the liquid is estimated by running in the salt solution from a graduated burette.

Mr. H. Pemberton titrates phosphoric acid by direct precipitation with a standard solution of ammonium molybdate in water, adding to the phosphate solution a considerable quantity of ammonium nitrate. The following is a condensed description of the *modus operandi* in performing the analysis.

89.543 grammes ordinary ammonium molybdate are put into a litre-flask, water added, and the whole shaken until the salt dissolves. If a cloudiness is left in the liquid, a little ammoniac hydrate is added. A small excess of this is not objectionable. The flask is then filled to the mark.

The above weight of the molybdate is calculated so as to give molybdic acid to phosphoric acid exactly as 24 : 1. Each c.c. precipitates 8 milligrammes of phosphoric acid. It differs from the figure obtained empirically by an amount equal to only 0.0008 gramme of phosphoric acid in an estimation of 0.1 gramme of phosphoric acid.

The phosphate to be examined is then taken in quantity containing not over 0.1 gramme of phosphoric acid or 0.15 gramme at the utmost. If silica is present the solution is evaporated to dryness. In presence of organic matter ignite gently and evaporate to dryness twice with nitric acid. There is no advantage in filtering off the silica. The solution is transferred to a beaker of 100 to 125 c.c., using as little water as possible to prevent unnecessary dilution, and is just neutralised with ammonia, *i.e.* until a slight precipitate is formed.

If much iron is present the ammonia is added until the yellow colour *begins* to change to a darker shade. Two c.c. of nitric acid are added. Care must be taken that the sp. gr. of the acid is not less than 1.4, otherwise more must be added. Ten grammes of granular ammonium nitrate are now added. After a little experience the quantity can be judged with sufficient accuracy by the eye without the trouble of weighing. The solution is now heated to 140° F. or over, and the molybdate solution run in (most conveniently from a Gay-Lussac burette), meanwhile stirring the liquid. The beaker is now left undisturbed for about a minute on the water-bath or hot plate, and the precipitate settles, leaving the supernatant liquid not clear, but containing widely disseminated particles, in which the yellow cloud can easily be seen on the further addition of the molybdate. This addition is continued as long as the precipitate is thick and of a deep colour. But as soon as it becomes rather faint and thin, a little of the solution, about 2 to 3 c.c., after settling of the precipitate, is filtered through a small filter (not over 5 c.m. in diameter) into a very small beaker, and this is heated on a hot plate, and 4 or 5 drops of the molybdate added. If a precipitate is produced, the whole is poured back into the large beaker and a further addition of the molybdate (1, 2, or 3 c.c.) added, according to the quantity of the precipitate in the small beaker. After stirring and settling, another small quantity is filtered through the small filter and again tested. If the mark has been overstepped and too much molybdate added, a measured quantity of phosphoric acid solution of known strength is added, and the corresponding amount of phosphoric acid deducted. In filtering through the small filter the liquid held sometimes in the neck of the funnel must be allowed to run out.

Volumetric Estimation of Phosphoric Acid by Means of Lead.—The phosphate is dissolved either in water or dilute nitric acid, and the solution mixed with excess of lead solution and sodium acetate. Tribasic lead phosphate precipitates; this is allowed to subside, is

washed and filtered, and the excess of lead in the filtrate ascertained by the volumetric process described at p. 347. Each c.c. of lead solution corresponds to 0.00476 grain of phosphoric acid.

The filtration and washing of lead phosphate is not so easy as in the case of lead sulphate, and may be avoided by allowing the precipitate to subside in a graduated vessel, and then removing a portion of the clear supernatant liquor by means of the pipette. By ascertaining the amount of lead therein contained, the whole amount may be calculated.

The presence of calcium does not interfere with these reactions, and bones, guano, or other manures may be analysed in this way without trouble. They are calcined to destroy organic matters, the residue washed, and any alkaline phosphates estimated in the filtrate, while the insoluble portion is dissolved in dilute nitric acid, filtered from the sand, &c., and excess of sodium acetate added. Iron and aluminium are precipitated on the addition of sodium acetate, and carry down with them some phosphoric acid. If iron oxide alone is present, the precipitated iron phosphate may be filtered off, dissolved in hydrochloric acid, reduced by zinc, and the iron protosalt estimated by potassium permanganate, when the iron peroxide will give by calculation the amount of phosphoric acid it was originally combined with in the precipitate. This may be safely done, as it is hardly ever probable that any manures contain excess of iron oxide.

0.247 gramme of sodium phosphate was mixed with calcium chloride, acetic acid, and sodium acetate, and 12 c.c. of lead solution added. The excess of lead in the filtrate amounted to 1.7 c.c. of potassium bichromate solution, which leaves $(12 - 1.7) 10.8$ centimetres of lead solution, or 0.049 gramme, or 19.88 per cent. of phosphoric acid: calculated it should have been 19.89.

0.8547 gramme of sodium phosphate and magnesium nitrate required 20 c.c. lead solution, 5 c.c. chrome solution, being equal to 0.0714 gramme, or 20.13 per cent. of phosphoric acid.

Volumetric Estimation of Phosphoric Acid in Superphosphates.—Mr. Burnard has also described another volumetric process, which is exceedingly simple and has afforded satisfactory results. It is not suitable in all cases, but may be applied to the estimation of the phosphoric acid in the great majority of the so-called superphosphates; its value being increased, moreover, by the fact that it necessarily involves the estimation of the free acid in the manure. Suppose a superphosphate made in the usual manner; in such a manure the bone phosphate may be measured by the quantity of sulphuric acid employed in its solution. Extract all that is soluble in water from 100 grains of the manure, and divide it into two equal volumes of 1,000 septems each, in beakers of the same dimensions. Into one drop a standard solution of sodium carbonate from a burette, when, as is well known, a precipitation of bone phosphate occurs; this, however, on

gently moving with a stirrer, is redissolved; continue to drop in until there is a faint trace of permanent precipitate, which may be the better detected by comparison with the other volume in the second beaker. When sufficient sodium carbonate has been added, then, after duly noting the number of septems employed, an additional septem may be dropped in, when a decided milkiness and agitation will be manifest. The number of septems thus employed is the measure of the free acid existing in the manure. A little practice will enable the operator to very nicely determine the point of incipient precipitation. Now throw in a piece of litmus-paper; if blue it instantly becomes red, and then continue the soda dropping until the red litmus becomes nearly blue. A few minutes' repose will allow sufficient time for the precipitate to somewhat settle down, leaving a clear space above; into this a drop of sodium carbonate solution may be carefully let down, when, if further precipitation occurs, more carbonate may be added, the whole stirred, and allowed again to subside. In practice it is found that the litmus should be brought to a decided but not to a deep blue. Now the further volume of the standard solution of sodium carbonate employed is the measure of the sulphuric acid economically employed in the manure, and is therefore the measure of the amount of the phosphoric acid in solution.

In comparative estimations, this process has given results nearly constantly $\frac{1}{2}$ per cent. too low.

Estimation of 'Reduced' Phosphates in Calcium Superphosphate.

In the analysis of calcium superphosphate for agricultural purposes, the money value is generally based upon the amount of phosphate present which is soluble in water. But it frequently happens that on keeping, a process of 'retrogression,' or going back, takes place; so that whilst a sample of freshly-prepared superphosphate may contain, say, 25 per cent. of soluble phosphate, the same sample after being kept for some time may only contain 22 or 23 per cent. It is impossible for the manufacturer to calculate the amount of this retrogression, and hence the discrepancies in the amount of soluble phosphate estimated by the seller and the buyer give rise to frequent disputes; and as from the nature of the action the seller's estimate must always be the highest, there is a tendency to throw discredit upon his analysis. The manufacturer considers it unjust that he should have expended time and money in producing soluble phosphate, which, owing to this retrograde action, is valued at only about one-third the price it ought to fetch; whilst the buyer, who measures the value of a superphosphate by the amount soluble in water, naturally objects to pay for more soluble phosphate than his analyst certifies is present.

To avoid these frequent disputes, it is becoming the custom to express the amount of this reduced phosphate in an analysis of super-

phosphate, and many methods have been proposed for the purpose of estimating it with accuracy. The point is to find some reagent which does not affect the undecomposed coprolite (that being the mineral now more especially considered); dilute acids, such as acetic, citric, and oxalic (the latter least so), are objectionable on this account. The best plan is that in which ammonium oxalate is employed. The process is carried out in the following manner:—Take about $1\frac{1}{2}$ grammes of superphosphate, extract the soluble part with cold water, and, afterwards, with boiling water; wash the insoluble residue on the filter into a beaker, boil for about half an hour with ammonium oxalate, and about two drops of oxalic acid, so as to have a slight acid reaction (this is done in order to keep the magnesium phosphate in solution). Then filter; the filtrate contains the calcium and magnesium phosphates, and, perhaps, a little iron and aluminium phosphate. To the filtrate add tartaric acid, ammonia, and the magnesia mixture, weigh the precipitate, and estimate the phosphoric acid as $\text{Ca}_3(\text{PO}_4)_2$; wash the insoluble residue on the filter into a beaker, boil for about 1 hour with ammonium sulphide and a few drops of ammonia, filter, &c.; to the filtrate add the magnesia mixture, and calculate the results in the same manner as the reduced calcium and magnesium phosphates.

Ammonium oxalate is used, as, being a perfectly neutral salt, it is altogether unlikely to decompose a perfectly mineralised substance like coprolite. As is well known, the decomposition of gelatinous calcium phosphate by ammonium oxalate is a quantitative reaction, which takes place at once, the only necessity for boiling being to assist the subsequent filtration. Boiling for 10 minutes is sufficient to effect this object, while the oxalate does not, under these circumstances, attack the coprolite to any material extent.

Mr. Sibson has tried the following experiments on this process:—25 grains of Cambridge coprolite are boiled, with an equal weight of ammonium oxalate, in 2 ounces of water, for 10 minutes, and filtered; the filtrate acidified with hydrochloric acid, and made alkaline with ammonia (merely to ensure the presence of ammonium chloride), and ammoniacal magnesium sulphate added. No precipitate will probably be obtained; but, *if it be obtained*, it is not conclusive of the presence of phosphoric acid; and great errors may be made if a precipitate in this place be accepted as magnesium and ammonium phosphate. After standing for 2 hours, the small precipitate is collected (which often resembles the phosphate closely, but consists of magnesium oxalate, which sometimes separates from a concentrated solution, and a little iron oxide) and redissolved in hydrochloric acid, citric acid added, and re-precipitated with ammonia. A precipitate, if now obtained, consists of magnesium and ammonium phosphate only, and, if burned and weighed as magnesium phosphate in the usual way, will be found to amount to less than 0.5 per cent., calculated as bone-earth. This was found to be the case with coprolite ground as

fine as it is possible to get it for analysis ; but with coprolite in the state usually employed by manufacturers, no weighable quantity of magnesium phosphate is found after standing 8 hours ; 0.5 per cent. of calcium phosphate is therefore the utmost error that can be made by this process under proper management.

In the case of a superphosphate containing retrograde phosphate, and treated as above, after having first extracted the soluble phosphate by cold water, the magnesium phosphate calculated as bone-earth will represent the phosphate so reduced.

Concerning the estimation of reduced or reverted phosphoric acid with ammonium citrate, Grupe and Tollens find that the calcium phosphates soluble in citrate are transformed into calcium citrate and ammonium phosphate, the former salt being soluble in an excess of the liquid. Not merely dicalcium, but to some extent tricalcium phosphate is dissolved if it has not been very strongly dried. Phosphoric acid in magnesium ammonio-phosphate cannot be estimated by this method. The solvent action of the citrate liquid is greater at 85° than at common temperatures. Three times the calculated quantity of magnesia mixture gives approximately accurate results. Crispo pronounces the method in need of improvement, and shows that the presence of calcium carbonate or magnesia in any form renders the phosphoric acid, which has been dissolved on treatment with ammonium citrate, insoluble again. Thus there is often found less phosphoric acid soluble in the citrate liquid than in water. M. P. Chastaign finds too low figures for the phosphoric acid in superphosphates in presence of magnesia. He proposes to extract first with water, and then to treat with ammonium citrate—a suggestion with which Petermann agrees. He wishes to confine the estimation of phosphoric acid soluble in water to dissolved guano and bone superphosphates. The 'Committee of the British Association on the Estimation of Phosphoric Acid in Commercial Products' consider that any known method of estimating the reduced phosphates is purely arbitrary.

Separation of Phosphoric Acid from Aluminium.

To the acid solution of aluminium phosphate add caustic soda in excess, digest for some time at a gentle heat, and separate the clear liquid by decantation and filtration. To the solution add barium chloride cautiously, till no more precipitate of barium phosphate is produced, then add sodium carbonate to remove the excess of barium, and lastly some more caustic soda ; warm and filter. The phosphoric acid will be in the precipitate as barium phosphate, together with barium carbonate, and the aluminium will remain in the filtrate, from which it may be separated in the usual way.

Another excellent method of separating phosphoric acid from aluminium is to add to the solution tin bichloride, boil, and precipitate all

the tin oxide in combination with phosphoric acid, by means of sodium sulphate. If iron sesquioxide is also present in the liquid a certain quantity will be precipitated at the same time.

Phosphoric acid may also be separated from aluminium by potassium silicate. To the acid solution containing aluminium phosphate add caustic soda in excess; digest for some time and filter; then add an excess of solution of potassium silicate, which occasions the formation of a bulky precipitate of aluminium silicate; collect this on a filter and wash. Acidify the filtrate with hydrochloric acid and supersaturate with ammonia to precipitate as far as possible excess of silica. Filter off and concentrate the solution, and add 'magnesia mixture.' This occasions the formation of a bulky precipitate, in part flocculent, in part crystalline. The whole is acidified with hydrochloric acid, which dissolves the crystalline and leaves the flocculent part of the precipitate. The liquid is filtered off, supersaturated with ammonia, and left 24 hours. The magnesium ammonio-phosphate which separates is highly crystalline.

Separation of Phosphoric Acid from Chromium.

Phosphoric acid in combination with chromium may easily be overlooked in following the method indicated in Will's tables, when chromic oxide and chromium phosphate are obtained simultaneously in solution with potash. On boiling this solution to precipitate the chromium, the phosphate is entirely decomposed, and not a trace of phosphoric acid is precipitated with the chromium oxide.

Separation of Phosphoric Acid from Bases in general.

A good method of separating phosphoric acid from bases consists in dissolving the substance to be analysed in a small quantity of nitric acid, and adding to the solution, first silver nitrate, then silver carbonate, and well shaking. All the phosphoric acid then combines with the silver oxide, and is precipitated, whilst the bases remain in solution and may be freed from the excess of silver by means of hydrochloric acid.

Separation of Phosphorus from Iron.

Mr. A. E. Haswell covers iron borings with a 7 per cent. solution of ammonio-cupric chloride in a well-corked flask, which is kept cool by being set in cold water. After digestion for 12 hours, with occasional shaking, the solution of ferrous chloride, which should be nearly free from copper, is carefully decanted off from the residue. The latter, containing, in addition to the spongy deposit of copper, all the negative elements of the iron, carbon, silicon, sulphur, and phosphorus, is repeatedly washed with distilled water. The turbid washing-waters are filtered, and the filter is dried and incinerated. The residue in the flask is oxidised by the gradual addition of strong nitric acid, and finally by the application of heat. When the reaction is over it

is rinsed into a capsule. The ash of the filter is then added, the solution is evaporated to dryness in the water-bath to eliminate silica, the soluble portion is filtered from the carboniferous silica, and the latter is purified by fusion with potassium-sodium carbonate, and again separated with nitric acid. The phosphoric acid in the second filtrate from the silica is precipitated by molybdic solution, and this precipitate is added to the main phosphoric precipitate. The deep blue filtrate from the carbon containing silica, which contains the main bulk of the phosphoric acid, is treated with molybdic solution in the usual manner. If the solution of molybdenum, prepared according to the formula of Lipowitz with ammonium nitrate, is used in presence of copper, the phosphoric acid is thrown down imperfectly or not at all.

M. E. Agthe finds that the precipitation with molybdic acid is a delicate point, and that the following precautions conduce to the greatest accuracy. Operating as below, 4 hours are amply sufficient, and a more prolonged contact is often the cause of defective results. If the analyst is pressed for time he may even filter after one hour.

Five grammes of the sample are dissolved, 50 c.c. of the molybdic liquid are added, the mixture is stirred frequently and filtered after 4 hours.

Under these conditions the estimation is exact when the proportion of phosphorus does not exceed 0.11 to 0.15 per cent. Beyond this range the result becomes uncertain. For a proportion of 0.43 per cent. 50 c.c. of the molybdic solution are required, as this reagent must always be in excess. In place of 50 c.c., 75 or 100 c.c. of the molybdic solution are employed, which is still suitable for proportions of phosphorus of 0.7 and 0.8 per cent. If the percentage is still higher, only 2 grammes or 1 gramme of the sample should be dissolved. The nitric acid should not be too concentrated or employed in excess, as it hinders complete precipitation. As far as possible the carbon should be burnt off, as the presence of this element renders the result too low.

If in the analysis of steel, white pig iron or manganiferous iron—in short, iron low in silica—this body is not separated, the result is too high. It is necessary, therefore, to filter before adding the molybdic acid, even in cases where no distinct precipitate of silica can be seen.

Before filtration the solution should be let take the ordinary temperature of 15° to 20°, otherwise the filtrate will become turbid and deposit a slight precipitate. The author operates as follows:—He dissolves 5, 2, or 1 gramme of the sample, according to its supposed richness, in 50 c.c. of nitric acid; he then evaporates to dryness and heats rather strongly, and to eliminate the last traces of nitric acid he evaporates a second time with hydrochloric acid. The residue treated with concentrated hydrochloric acid is taken up in water, and the silica which remains insoluble is separated by filtration. The liquid is evaporated again over a naked flame in a porcelain capsule as long as the ferric chloride which is deposited on the sides of the vessel redis-

solves on inclining the capsule, and the process is then continued on the water-bath to incipient solidification. This operation requires to be watched, for if there remains too much hydrochloric acid the results are too low; if, on the contrary, too much acid is driven off and hard crusts are formed, we do not obtain a clear solution with nitric acid.

After cooling, we add 35 c.c. of ammonia (0·96) and mix with the stirrer, so as to obtain a homogeneous paste, and add 75 c.c. nitric acid (1·12 to 1·2), and the whole is set on the water-bath. When the solution is complete the liquid is transferred into a precipitating glass, and from 50 to 180 c.c. of the molybdic solution are added and the whole is kept at a temperature of 50° to 80°, stirring frequently. After 4 hours it is let cool, filtered, and washed with dilute molybdic liquid. The author recommends the following proportions for the preparation of the molybdic solution:—115 grammes of molybdic acid are dissolved in 460 grammes ammonia (0·96), and made up with water to 1 litre. This solution is then poured into 1 litre nitric acid at sp. gr. 1·2, and the mixture is let stand for a day and filtered.

When the phosphomolybdic precipitate has been sufficiently washed it is dissolved in the smallest possible quantity of ammonia; the ammoniacal solution is neutralised with hydrochloric acid up to the point where the precipitate produced by this reagent is redissolved very slowly, and when cold it is mixed with 15 to 25 c.c. of magnesia mixture, stirred well, and filtered after standing for 6 hours. The precipitate is washed with ammoniacal water, dried, calcined, and weighed.

The author prepares his magnesia mixture as follows:—

Magnesium chloride	100
Ammonium chloride	200
Ammonia (sp. gr. 0·96)	400
Water	1000

It is well to ascertain that the mother liquors from the ammonium phosphomolybdate, when mixed with ammonia slightly heated, do not give a further precipitate; in the contrary case the analysis would be inaccurate. It may, however, be completed by neutralising as far as possible with ammonia, adding molybdic liquid, and adding the second precipitate to the former.

The following are the processes referred to at page 196:—

Sir F. Abel's Process.—Fifty grains of iron borings are acted on with warm nitrohydrochloric acid in a flask with a long neck, and after complete solution of the metal the contents of the flask are transferred to a porcelain basin and evaporated to dryness; the residue is moistened with concentrated hydrochloric acid and again evaporated, so as thoroughly to expel nitric acid. The residue thus obtained is dissolved in hydrochloric acid, the solution diluted, filtered, nearly neutralised with ammonium carbonate, and the iron in solution reduced to protoxide by the addition of ammonium sulphite to the gently-heated

pletely subsided, which will take place in about three hours. The clear fluid is then filtered, the precipitate washed by decantation and otherwise, dried, and ignited, care being taken that no caustic lime is formed.

(d) **Separation of Magnesia.**—To estimate the magnesia in the solution from the calcium oxalate, the ammonia salts must be removed by evaporating it to dryness and igniting the residue, which will leave only magnesia and molybdic acid. It is digested with a little nitric acid to dissolve the magnesia, and then neutralised with an excess of ammonia to render soluble the molybdic acid. To the clear solution sodium phosphate is added, and the magnesia removed as magnesium ammonio-phosphate.

As nearly all mineral phosphates contain only a few tenths of a per cent. of magnesia, it would perhaps be preferable to take a fresh portion of the acid solution of the mineral, and separate the lime as oxalate, evaporate the filtrate to a small bulk, add ammonia, then acetic acid, and remove the ferric oxide and alumina as phosphates; then render the fluid alkaline, and allow to stand for some time, when the small quantity of magnesia will be deposited as magnesium ammonio-phosphate.

This plan of separating phosphoric acid, ferric oxide, and other bases, is simple and easy, as it involves only operations of the most elementary kind, and it avoids the use of sulphuretted hydrogen. It is very expeditious: the bodies may all be separated in about twelve hours, and even this time may be shortened if the separation of the phosphoric acid, ferric oxide, and alumina in one portion of the acid solution, and the lime and magnesia in another, are gone on with simultaneously. Although the solution from the ammonium phosphomolybdate containing the bases is of considerable volume, it may be filtered very rapidly from the ferric oxide and alumina, and then from the calcium oxalate, if the precipitates are allowed to settle properly. The method is also highly accurate; the phosphoric acid is estimated by a process which may be placed in the front rank for delicacy and correctness, and the other bodies are got with all desirable precision.

For the separation of phosphoric acid from ferric oxide and alumina, Dr. W. Flight boils the solution containing the alumina, iron, and phosphoric acid, and which should not be very acid, for two or three hours with excess of sodium thiosulphate. All the alumina with a part of the phosphoric acid is precipitated, whilst the iron with the rest of the phosphoric acid remains in solution. From this solution the iron is at once precipitated by ammonium sulphide, and converted into ferric oxide, whilst the alumina and phosphoric acid in the precipitate are separated by treatment with excess of caustic soda and barium chloride, which precipitates the phosphoric acid in combination with the barium, whilst the alumina remains in solution. In washing the precipitate a few drops of soda solution must be added to

the wash-water, as the phosphate is decomposed by pure water. This phosphate is then decomposed by sulphuric acid, and the phosphoric acid estimated in the usual way.

In the analysis of native iron and aluminium phosphates the following precautions are suggested:—1. The total water (=loss by ignition) should be estimated by igniting the whole or a large portion of the sample previously crushed as rapidly as possible to the size of peas, but not on any account ground. 2. The only method suitable for the estimation of phosphoric acid is the ammonium molybdate process, soluble silica having been previously removed.

For the estimation of alumina and iron in phosphates M. A. Esilman proposes a process founded on the fact that, in the presence of an excess of sodium thiosulphate and acetic acid, alumina phosphate precipitates in the tribasic form of constant composition at the boiling temperature. The precipitate is mixed with sulphur, easily washed, and on ignition the sulphur burns off, leaving pure phosphate, 122.5 parts of which are equal to 51.5 parts of alumina. Of course the presence of excess of phosphoric acid must be ensured. All our present methods involve the previous separation of the phosphoric acid, necessitating in most cases operating on very small quantities and delicate working; but the one under notice is applicable whatever be the quantities of phosphoric acid, iron, lime, or magnesia present. This process is, in fact, most commonly used for estimating small quantities of alumina in presence of large proportions of phosphoric acid, where the molybdic method proposed by Ogilvie would be almost impracticable.

One defect of it is the invariable precipitation of traces of iron with the aluminium phosphate; but the following test results, performed under very varying circumstances, show that its accuracy thereby is not materially impaired. The solution ought to be dilute and not very hot, and should contain a tolerable amount of free acid. An excess of sodium thiosulphate is added, then acetic acid in liberal excess. Ten or fifteen minutes are allowed for the complete deoxidation of the iron, and then the solution is boiled for about the same length of time. The filtration and washing of the precipitation are done hot and rapidly, and after drying the latter is ignited in a porcelain crucible.

The iron can be estimated in the filtrate from the aluminium phosphate after decomposition of the thiosulphate by boiling with excess of hydrochloric acid; but it is better to employ a separate portion for that object. For reducing the peroxide by metallic zinc or tin protochloride an excess of ammonium sulphide is employed; the excess is decomposed by hydrochloric acid, and the sulphuretted hydrogen is easily and completely driven off by ebullition. This plan is more expeditious than when zinc is used, and more accurate than the tin method.

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Separation of Phosphoric Acid from Silica and Fluorine.

In the estimation of silica in fluoriferous phosphates, especially apatite and phosphorite, losses are often experienced when the separation of silica is effected by digesting or evaporating the sample with concentrated hydrochloric or nitric acid, as considerable quantities of siliconfluoride gas are volatilised. This loss is avoided or brought to a minimum if the calcium phosphate and fluoride is dissolved by gently heating in strongly-diluted hydrochloric acid, the solution separated from silica by decantation, and the latter substance afterwards perfectly freed from ferric oxide by digestion in concentrated hydrochloric acid. Dr. Gilbert digests 2 grammes of powdered apatite in a platinum capsule with 50 c.c. of dilute hydrochloric acid (1 part acid at sp. gr. 1.12 with 10 parts of water) for ten minutes on the water-bath, decants the solution through a filter, treats the residue once more in the same manner, and finally dissolves the last traces of iron by heating with concentrated hydrochloric acid, collecting the silica upon the filter which has been already used. The fluorine present in phosphorite was calculated from the lime, and was as a check estimated by Penfield's method. For this purpose 5 grammes of finely-ground phosphorite were mixed in a platinum crucible with 10 grammes of powdered quartz, the mixture ignited, placed in the apparatus along with 50 c.c. of concentrated sulphuric acid and distilled. The alcoholic solution of potassium chloride was placed, not in a U-tube, but in a Bunsen's washing-bottle containing a little mercury, into which the delivery tube dipped. A second washing-bottle, containing a similar solution, was connected as a matter of precaution, but the decomposition was completely effected in the first. The liberated silica was equally diffused in the liquid. Prof. E. W. Atkinson has refuted the assertion that the presence of silica does not interfere with the estimation of phosphoric acid by the molybdc method.

Preparation of Phosphorous Acid.

Phosphorous acid is a useful reducing agent, and has been recommended in previous chapters as one of the reagents to be employed in the separation of metals from one another. It is prepared in a sufficiently pure state for this purpose as follows :—Introduce a number of separate sticks of phosphorus into glass tubes an inch long, open above and below, but drawn out funnel-shaped at the bottom, these tubes being arranged in a funnel, and the funnel inserted into a bottle which stands in a dish containing water. The whole arrangement is covered with a bell-jar, but in such a manner as to give access to the external air, which, however, should not be very warm. The acid which collects in the bottle is equal to about three times the weight of the phosphorus consumed. It is a mixture of about 1 atom of phosphorous acid and 4 atoms of phosphoric acid.

Detection of Phosphorous Acid.

For detecting phosphorous acid in phosphoric acid Dr. Reickher adds a slight excess of mercuric chloride, and heats to 80°.

Estimation of Phosphorous Acid.

MM. Prinzhorn and Precht find that phosphorous acid can be very conveniently and accurately estimated by means of mercuric chloride. The phosphite is dissolved in hydrochloric acid, an excess of the chloride is added, and the whole is heated in the water-bath till mercurous chloride is rapidly and completely deposited, for which about two hours are requisite. When the filtrate no longer becomes turbid, even at a full boil over the open flame, the deposit is collected upon a tared filter, dried at 100°, and weighed. If the filtrate is then freed from mercury by the passage of sulphuretted hydrogen, and from other bases which interfere with the estimation of phosphoric acid, the latter may be thrown down with magnesia mixture, thus furnishing a way of checking the result.

NITROGEN.

Estimation of Nitrogen by Weight.

Bunsen has given a method of analysing nitrates and nitrites which renders it possible to estimate all the constituents of the salt in a single analysis. This method consists essentially in igniting the salt in an atmosphere of nitrogen gas, absorbing the oxygen evolved by metallic copper, and collecting the water in a calcium-chloride tube. The nitrogen in the salt is given by the loss of weight in the apparatus.

In those analyses of nitrates or nitrites in which it is only desired to estimate the nitrogen, Dr. Wolcott Gibbs recommends the following modification, which may be employed with advantage:—

A hard glass tube about six inches in length is sealed at one end, and its volume estimated by filling it with mercury and pouring this into a graduated vessel. The tube is to be carefully dried and weighed with a good cork; it is then to be filled with finely-divided metallic copper, prepared by the reduction of the oxide, so as to enable the operator to judge of the quantity necessary. The salt to be analysed is then weighed and mixed with the metallic copper, either in a mortar or with a mixing-wire in the tube, and the tube with its contents and cork is again weighed. The weight of the copper employed is thus known, and its volume may then be found by dividing this weight by the density of metallic copper. A weighed calcium-chloride tube is then adjusted as in organic analysis, and the combustion tube is heated in the usual manner. When the combustion is finished, the open end of the calcium-chloride tube is sealed with the blowpipe flame, and the combustion-tube allowed to become perfectly cold. The chloride tube

is then removed and weighed, and the combustion-tube also weighed with its cork. The increasing weight of the calcium-chloride tube gives the amount of moisture in the copper and the water in the salt analysed. The loss of weight in the combustion-tube gives the nitrogen in the salt after correction for the oxygen in the tube, for the moisture in the copper, and for the water in the salt. The correction for the oxygen in the combustion absorbed by the copper is easily found, with a sufficiently close approximation, by subtracting the volume of the copper from that of the tube, finding the weight of the residual air, taking one-fifth of this as oxygen, and considering the whole of this oxygen as absorbed by the copper. A piece of asbestos may be placed between the copper and the cork with advantage; but this renders an additional correction necessary.

In two analyses executed by this method—in the first, a sample of pure saltpetre gave 18·86 per cent. nitrogen, theory requiring 18·86 per cent; in the second, a specimen of the commercial salt gave 18·7 per cent. nitrogen, while the same salt analysed by Simpson's method, in which the volume of the nitrogen is estimated, also gave 18·7 per cent. The whole analysis, with the weighings, may easily be executed in an hour and a half by a single person. It is easy to see that this method applies to all inorganic nitrates and nitrites, whether hydrated or anhydrous, but that it cannot be employed in the case of organic or ammoniacal salts. In the analysis of inorganic nitrates or nitrites by Simpson's method, it is not necessary to use mercury oxide to prevent the formation of nitrogen deutoxide. In all such cases it will be found sufficient to mix the salt with pure metallic copper. In this manner the dimensions of the combustion-tube may be greatly diminished. It is also advantageous to exhaust the air from the combustion-tube before disengaging carbonic acid from the manganese carbonate. By alternately pumping and filling the tube with carbonic acid, the air may be completely expelled before the combustion commences. It is also better to draw the tube out before a Bunsen's blowpipe, as it is difficult to make a cork and india-rubber connector perfectly tight. With a little practice the drawing out is easily effected even with the hardest combustion-tubes.

Detection of Nitric Acid.

The following test, proposed by Mr. Blunt, for the presence of nitrates in a drinking water is a little more delicate than the common one with ferrous sulphate; it depends on the reducing action exercised by sodium amalgam on nitric acid.

When a moderately concentrated solution of potassium nitrate is poured over a sodium amalgam containing about $\frac{1}{2}$ per cent. of the metal, there is no evolution of hydrogen, and on pouring off the supernatant fluid after some minutes, and applying the Nessler test, a considerable quantity of ammonia may be detected. A solution of pure

potassium nitrate, containing $\frac{1}{30}$ grain of the salt, gives a just perceptible colouration with the Nessler test after standing over a $\frac{1}{2}$ per cent. amalgam for about 12 hours; $\frac{1}{15}$ grain of the salt gives a marked reaction. Several attempts have been made to adapt the above test to the estimation of small quantities of nitric acid; they have at present, however, been unsuccessful, through the impossibility of pushing the reaction to completion. It is possible, however, that a system of comparative testing analogous to that at present adopted in the case of ammonia may lead to some results. As an example of the mode of applying the test qualitatively to a drinking water, the following account may be given of an actual experiment:—

To 2 oz. of a water known to contain a trace of nitrates was added about 100 grains of a solution of potassium hydrate containing $\frac{1}{12}$ of its weight of alkali; the whole was then evaporated nearly to dryness; thus any ammonia already existing in the water would be expelled. The residue was exhausted with distilled water which gave no reaction with the Nessler test, and the quantity of the solution made up to 200 grain measures, which were afterwards divided into two equal portions. One was at once tested with ferrous sulphate solution and sulphuric acid; a very faint brown colouration appeared at the point of junction of the layers of liquid, increasing considerably after a few hours.

The second portion was introduced into a carefully-cleaned test-tube, with about 200 grains of $\frac{1}{2}$ per cent. sodium amalgam; the tube was lightly corked to check, as far as possible, diffusion of the ammonia formed, but not so tightly as to prevent the egress of the hydrogen, which in dilute solutions of a nitrate is always evolved from the amalgam. The whole was left for about 12 hours; the liquid was then rinsed with successive portions of pure distilled water into a glass cylinder about 6 inches high and 1 inch wide, and the quantity was made up with distilled water to about 1000 grains. On adding about 15 grain measures of the Nessler test, a very strong colouration, accompanied by incipient precipitation, at once appeared. It is to be remarked that the liquid must always be decanted from the amalgam before applying the Nessler test, as the presence of nascent hydrogen appears to interfere with the action of the latter.

M. F. Bucherer gives a process which he states will detect $\frac{1}{100000}$ of a nitrate in aqueous solution. It is founded on the action of nitrous vapours on potassium iodide; the potassium is oxidised by the oxygen of the nitrous vapours, which are thereby reduced to the state of binoxide, and iodine is set at liberty. For the test to be conclusive, any chlorine or bromine must have been separated from the liquid. The author places 8 or 10 grammes of the liquid to be tested in a tube 6 or 8 inches long, introduces a few copper turnings, and 8 or 4 drops of strong sulphuric acid. Then boil for a moment and nearly fill up the tube with water; now add a few drops of a solution of potassium iodide. If the liquid contains any nitrate the iodine is set at liberty,

and on adding a small quantity of carbon disulphide and shaking vigorously, the sulphide will dissolve the iodine and float on the surface of the liquid, taking a violet or deep red colour, according to the quantity of iodine displaced.

To detect free nitric acid operate as above, but omit the sulphuric acid. To detect a nitrite use the same method with the omission of the copper.

Estimation of Nitric Acid by the Oxidation of an Iron Proto-salt.

This is commonly known as Pelouze's method. The weighed nitrate is boiled out of contact with air with a solution of iron protochloride and an excess of hydrochloric acid. Under these conditions the nitric acid splits up on the one hand into oxygen, which converts the iron proto-salt into a per-salt, and on the other into a lower oxide of nitrogen, which escapes. The requirements of this process are, firstly, that the decomposition of the nitrate shall take place in an atmosphere of which oxygen does not form a part, and, secondly, that such decomposition shall be complete.

In the ordinary mode of conducting this process the operation takes place in a retort, through which a current of hydrogen is passed. Attached to the stem of the retort is a U-tube, containing a little water, which serves as a lute to prevent access of air.

Mr. Holland has modified this arrangement so that the operation is conducted *in vacuo*, and at its expiration the solution is boiled to expel the nitric oxide, thus avoiding the necessity of employing either hydrogen or carbonic acid.

In the accompanying sketch, A is a long-necked assay flask drawn out at B so as to form a shoulder, over which is passed a piece of French india-rubber tube, D, about 6 centimetres long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the elastic connector D is placed a screw compression-clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with the blowpipe a piece of glass tube about 2 centimetres long, surmounted by one of French tubing rather more than twice that length. The elastic tubes must be securely attached to the glass by binding with wire. After binding, it is as well to turn the end of the connector back and smear the surface with fused caoutchouc, and then replace it. This advice is given by Dr. Sprengel for securing an air-tight joint. The wooden clamp E gives support to the flask; the rest of the arrangement requires no explanation.

The analysis of a nitrate is conducted as follows:—A small funnel is inserted into the elastic tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water, which washes all into the flask, the funnel is removed, and the former placed in the inclined position it occupies in the figure.

The contents are now made to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c. When this point is reached, a piece of glass rod is inserted into the elastic tube at c, which causes the water vapour to find egress through F.

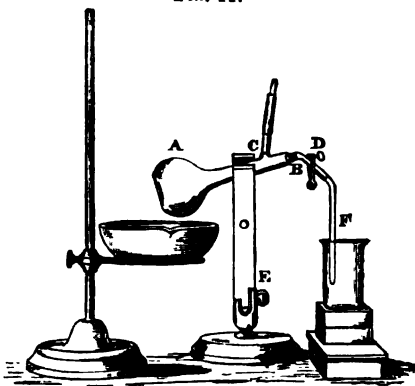
Into the small beaker is put 50 c.c., more or less, of a previously boiled solution of iron protosulphate in hydrochloric acid. (The amount of iron already existing as a persalt must be known.)

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the caoutchouc connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it; when the whole has nearly receded the elastic tube is tightly compressed with the fingers, whilst the sides of the beakers are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than necessary or admit air. Whilst F is still full of water, the elastic connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion of the flask.

After heating at 100° C. for half an hour, the flask is removed from the water-bath and cautiously heated with a small flame, the fingers at the time resting on the elastic connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation the beaker is first removed, and then the lamp.

It now only remains to transfer the solution of iron to a suitable vessel, and estimate the perchloride with tin chloride in the usual way, or with copper subchloride (see p. 187).

FIG. 11.



The process is easy of execution, and gives satisfactory results. The points requiring attention are that the apparatus should be capable of retaining a sufficiently perfect vacuum during the operation; this condition is fulfilled by the use of a suitable elastic tube and clamps. What is known as French tubing serves the purpose well: its sides are thick, and its material free from metallic oxides.

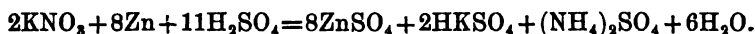
It is advisable when making the digestion at 100° to place the flask in cold water, which is afterwards raised to the boiling-point; if, on the other hand, the flask is heated at once, a violent bumping ensues, and portions of the liquid are projected into the tube at c.

Dr. A. Wagner's process for the estimation of nitric acid is based upon the fact that when saltpetre or any other nitrate is ignited, access of air being excluded, with an excess of chromic oxide and sodium carbonate, the nitric acid oxidises the chromic oxide. 76.4 parts, by weight, of chromic oxide are oxidised to chromic acid by 54 parts of nitric acid (N_2O_5), or 1 of chromic oxide by 0.7068 of nitric acid. The operation is performed by taking from 0.8 to 0.4 gramme of the nitrate, mixing it intimately with 8 grammes of chromic oxide and 1 gramme of sodium carbonate, introducing this mixture into a hard German glass combustion-tube, one end of which is drawn out, and a vulcanised india-rubber tube attached to it, which is made to dip for about a quarter of an inch into water, while to the other open end, by means of a cork and glass tube bent at right angles, an apparatus is fitted for the evolution of carbonic acid gas, which is made to pass through the tube before igniting it, and kept passing through all the time till the tube is quite cool again after ignition. The contents of the tube are placed in warm water, and after filtration the chromic acid is estimated by Rose's method. This process of estimating nitric acid, having been tested by the author with various nitrates, has been found to yield very accurate results.

Schlöesing employs the following process:—The nitrate mixed with ferrous chloride and hydrochloric acid is introduced into a very small tubulated retort, the extremity of which dips under mercury. The air is expelled by a stream of carbonic acid. The retort is then boiled for eight minutes, and the gas evolved collected in a small jar containing caustic potash. This nitric oxide is converted into nitric acid by treatment with water and oxygen, and finally titrated with alkali. The method fails, however, with extremely small quantities of nitrates and in the presence of certain kinds of organic matter. The prejudicial effect of the organic matter is removed to some extent by boiling the contents of the retort to dryness, but with very small quantities of nitric acid the results are still too low. The author has been able to estimate 98 to 100 per cent. of the nitrogen, even when half a milligramme of nitrogen as nitre was used. Perfect exclusion of oxygen from the apparatus is essential. This is effected by mixing the hydrochloric acid used in the carbonic acid generator with cuprous

chloride, and protecting its surface with a layer of oil. The carbonic acid is always kept under pressure, so that any leak must be outwards. The nitric oxide is estimated by gas analysis, preference being given to absorption over caustic potash, after successive treatments with oxygen and pyrogallol. In the introduction of the oxygen a gas delivery-tube invented by Professor Bischof was found of great service. It consists of a test-tube, with a minute perforation about half an inch from the mouth. The tube, being filled with gas, has its mouth closed by an india-rubber cork, through which passes a short glass tube with a fine orifice. On tilting the tube under mercury, with the perforation downwards, minute bubbles of gas rise from the perforated stopper closing its mouth, and thus the quantity added can be regulated with great accuracy.

J. Boyd Kinnear reduces nitric nitrogen to ammonia by the action of zinc in a very dilute acid solution. The point of dilution may for practical purposes be taken as one of nitrogen (nitric) in five thousand of water, though the reaction will often be found perfect in solutions of twice or three times this strength. The necessary proportions of zinc and acid are indicated by the equation (supposing potassium nitrate and sulphuric acid to be employed)



But it is advisable to use at least a half more of sulphuric acid than is required by the formula, and the larger the surface of zinc the more quickly is the reaction completed. Hydrochloric acid answers as well, and iron might be substituted for zinc but for its liability to contain occluded nitrogen. When only a slight excess of acid is used the action is slow and the evolution of hydrogen trifling, but by employing a moderate excess of acid and nearly filling the vessel with granulated zinc, the evolution of gas is rapid, much heat is produced, and the conversion into ammonia is often complete in ten minutes. In all cases the process must be stopped by pouring off the acid liquid and washing the zinc before the acid is fully saturated.

Besides rapidity and simplicity another advantage is that in many cases the resulting ammonia may be at once estimated in an aliquot portion by the Nessler process. For this purpose care must be taken that the zinc and sulphuric acid are both pure, and that substances which give coloured iodides are absent. Lime and iron, which most frequently occur in ordinary analyses, may be previously precipitated by oxalic acid and potash. When the quantity of zinc dissolved is small, the addition of the Nessler solution causes no precipitate; but when it does, the zinc may be first precipitated and redissolved by solution of potash. Very rapid and often sufficiently accurate estimations may thus be arrived at; but of course other methods of estimating the ammonia are equally available.

The reaction between the nascent hydrogen and the nitrates and

nitrites appears to be quite without effect on organic nitrogen, so much so that the nitric acid in urea nitrate may be thus estimated without the urea being decomposed. The advantage of this in examinations of juices of plants, water, and manures, need not be pointed out. When the quantity of the material available is small, it is also an advantage that the same solution may serve for the successive estimations, first of the ammonia already formed, next (directly or by difference) of the nitric nitrogen, next of so-called 'albuminoid ammonia,' and lastly by combustion of the total nitrogen, without risk of results of each process overlapping the other and thus giving too high a result.

Estimation of Nitric Acid in Commercial Nitrates.

M. F. Jean recommends the following procedure:—Into a small glass flask holding about 200 c.c. introduce a concentrated and very acid solution of ferrous chloride. The flask is closed with an india-rubber stopper pierced with a hole, through which pass a delivery-tube under a leaden shelf in a tank of water lined with lead, and a very short tube, to which is fixed a small funnel by means of a flexible caoutchouc tube, the communication with the flask being intercepted by means of a Mohr's spring clip or a small glass tap. The trough being filled with water, the ferrous chloride is raised to a boil, and, as soon as the sound made by the condensation of the acid on the water of the trough announces that a vacuum has been made in the flask, a gas-jar filled with water is placed over the opening in the shelf. The jar should be of the capacity of 200 c.c. graduated in tenths. Then pour in the funnel 5 c.c. of a solution of sodium nitrate, formed by dissolving in a litre of water 66 grammes of pure sodium nitrate recently melted at a low temperature. The solution of ferrous chloride being kept at a boil, the solution of nitre is allowed to enter the flask drop by drop, taking care not to empty the funnel completely. 2 to 3 c.c. of distilled water are then placed in the funnel and allowed to enter the flask, and finally the funnel and the tube are rinsed with 5 to 10 c.c. of fuming hydrochloric acid. The nitrogen binoxide produced by the decomposition of the sodium nitrate enters the graduated jar. and as soon as the sound announcing the presence of a vacuum in the flask is heard, the graduated jar is withdrawn and allowed to stand on a support in the trough. This first operation makes known the volume of gas obtained from a known weight of nitre, without its being needful to take account of the corrections for temperature, pressure, &c. Into the flask are then introduced 5 c.c. of a solution of the nitre in question in 100 c.c. of distilled water, and the salt is decomposed. This solution is made by dissolving 6.6 grammes in the same manner as the foregoing, and the nitrogen binoxide is collected in a second graduated jar. The two jars are kept till they have acquired the same temperature and the respective volumes of gas produced are read off,

care being taken to keep them immersed so that the water may stand at the same level within and without. The volume of gas produced by a given weight being thus known, the proportion of real nitre existing in the sample under examination is readily calculated.

Estimation of Nitric Acid when in the Free State.

Nitric acid dissolved in water is most easily estimated by acidimetric processes. It has been proposed to evaporate the acid liquid with a given weight of lead oxide; but lead oxide forms with nitric acid various insoluble basic combinations, which retain a certain quantity of water at 160°, and attract atmospheric carbonic acid. Lead oxide may be advantageously replaced by baryta water and barium carbonate.

Estimation of Nitric Acid when Combined with Heavy Metals.

The nitrates of metals precipitable by sulphuretted hydrogen being first decomposed by this reagent, the nitric acid can be estimated in the liquid by baryta, the excess of sulphuretted hydrogen being previously eliminated by copper sulphate. Barium sulphide does not well take the place of sulphuretted hydrogen; there is a risk of the formation of thiosulphates, which might interfere with the estimation.

Estimation of Nitric Acid when Combined with any Base.

Nitric acid in combination may be estimated by distilling with dilute sulphuric acid, and estimating the nitric acid in the distillate. Two litres of the solution are boiled down to about 200 c.c., and during evaporation pure potassium permanganate is added (the object of which is to convert nitrites into nitrates), until a permanent pink colour is obtained. The concentrated liquid is filtered, pure sulphuric acid added, and distilled into a flask containing barium carbonate suspended in water. The distillation is interrupted when sulphuric acid begins to go over. The contents of the receiver are filtered, and in the filtrate which contains barium nitrate and chloride the barium is estimated in the usual manner. The amount of chlorine being known from a separate experiment, all data are given for the calculation of the quantity of nitric acid present in the 2,000 c.c. of water.

The error caused by the oxidation of ammonia to nitrous and nitric acid is inappreciable.

Instead of collecting the nitric acid in barium carbonate, a standard caustic alkaline solution may be employed. A very good method consists in distilling nitrates with sulphuric acid diluted with twice its volume of water. The operation is conducted at a temperature not above 70° or 80° C. in a retort with the neck drawn out and bent so that by means of an india-rubber tube it may be connected with a little receiver with three bulbs, containing a known volume of a stan-

dard solution of soda or potash. The distillation must be continued for three or four hours to obtain 1 or 2 grammes of nitrate. The distillation may be effected by a water-bath in a vacuum, either by means of an air-pump or by expelling the air from the apparatus by boiling, and then closing hermetically. If the nitrate is mixed with chloride, a solution of silver sulphate or moist silver oxide is added previous to distillation.

Estimation of Nitric Acid by Fusion or Calcination.

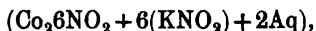
Nitric acid may be estimated by difference in some salts decomposable by calcination, unless the production of a higher oxide of the base may occur. Nitric acid may be driven off by sulphuric acid, the weight of the sulphate being deducted from that of the nitrate.

Nitrates with strong bases are transformed into chlorides by calcination with ammonium chloride.

Nitrates may also be decomposed by fusion with borax, or, better still, with potassium bichromate. The crucible is weighed with the alkaline nitrate, and heated sufficiently to melt the nitrate; potassium bichromate is added after cooling (2.25 of bichromate for 1 nitrate); the whole is gently heated and weighed. The crucible is then gradually heated to dull red heat, and weighed after cooling. The difference gives the weight of nitric acid. Neither chlorides nor sulphates are decomposed under these conditions.

Detection of Nitrous Acid.

Thomas M. Chatard has reviewed all the tests given for this acid, comparing their relative degrees of delicacy, with the following results:—For testing a very dilute solution of Fischer's salt,



which contained $\frac{1}{100000}$ part by weight of nitrous acid, was employed.

Schönbein's test with a weak solution of indigo decolourised by potassic sulphide failed to give accurate results. Besides, there are many substances which would have the same action upon the decolourised indigo as the nitrous acid.

C. D. Braun's test with cobaltous chloride and potassic cyanide gave no reaction with so dilute a solution, even when several cubic centimetres were taken, the reaction only appearing when a comparatively strong solution of the nitrite was used.

Hadow's reaction, in which a nitrite, when heated with prussic acid, is detected by an alkaline sulphide, gave good results only when the nitrous acid was present in larger quantities, not being delicate enough to give a reaction with the standard solution of nitrite employed.

A modification of this test suggested itself, in which the nitroprussic acid is thus produced. To the solution suspected to contain the acid, potassium ferrocyanide and acetic acid are added, and the

whole boiled. The solution is allowed to cool, and ammonium sulphide added. If nitrous acid was originally present, the characteristic blue reaction will appear. 10 c.c. of the test solution gave the reaction, but it failed with a smaller quantity.

The problem was finally solved by another reaction, namely, the production of phenol from aniline by means of nitrous acid. Evaporate the test liquid nearly to dryness, then rub it with a few drops of a strong solution of aniline sulphate. If nitrous acid is present, the odour of phenol will immediately result. This test is remarkably delicate, 1 c.c. of the test solution giving a perfectly distinct reaction. Nor can nitrous be confounded with nitric acid, as this last produces no phenol, but merely a yellow colour, which of itself, as is well known, is of value as a test for that acid.

Dr. A. Jorissen proposes the following test for nitrous acid :—

Dissolve 0.01 gramme magenta in 100 c.c. glacial acetic acid, place 2 c.c. of this solution in a small porcelain capsule, and add a trace of solid potassium nitrite. The liquid turns successively violet, blue, green, and finally yellow. Nitrates are without action upon the reagent. If there be added to the test liquid free mineral acids, the mixture takes finally a yellow colour, but this is due to the formation of a tri-acid rosaniline salt, and the characteristic red colour of rosaniline can be reproduced by the addition of water. When the change of colour has been occasioned by nitrous acid, the original colour cannot be restored by the addition of water, but the liquid remains yellow.

If it is desired to detect a nitrite in a liquid, it is concentrated, or by preference evaporated to dryness. When cold a suitable quantity of the reagent is added, when the characteristic play of colours is produced if a nitrite be present. The evaporation to dryness serves to render the reaction more sensitive, as it succeeds better the more concentrated the acetic acid.

In searching for minute traces of nitrous acid the quantity of magenta dissolved in the glacial acid may be proportionally decreased by, *e.g.*, mixing 1 c.c. of the reagent as described above with 9 c.c. of glacial acetic acid.

This new reagent may be used for the detection of nitrous acid in natural waters in Fresenius's method of distilling with glacial acetic acid. For this purpose 1 c.c. of a solution of 0.5 gramme potassium nitrite in 1 litre of water is added to 100 c.c. of water. This liquid, which contains 0.0005 gramme of the nitrite, is mixed with acetic acid and introduced into a small retort connected with a receiver containing a mixture of 9 c.c. glacial acetic acid and 1 c.c. of the test liquid (the solution of 0.01 gramme magenta in 160 c.c. glacial acetic acid). A few drops of the distillate suffice to produce the above-described change of colours in the receiver.

Estimation of Nitrites.

(a.) **When a Considerable Quantity is present.**—In this case the following processes devised by Mr. Tichborne will be found very successful. The first process is based upon the reduction of chromic acid to chromic oxide by nitrous acid. In analysing a specimen of commercial sodium nitrite, the mode of procedure is as follows:—If the sample contains sodium carbonate, a weighed quantity, say 2 grammes, is dissolved in a rather considerable quantity of water, and the carbonate present estimated by a standard solution of sulphuric acid, carefully avoiding an excess. To hit the exact point of saturation, soak a piece of good litmus-paper in the solution after the addition of each quantity of acid from the burette, and on drying it the exact state of the solution is perceived. A convenient indicator of the point of saturation in this case will be found in a solution of starch and potassium iodide contained in a test-tube; one drop of the solution of nitrite added after each addition of acid will, when the carbonate is all decomposed, strike a blue shade on falling through the starch solution. After noting the amount of carbonate, the solution is in a fit condition for the estimation of the nitrite; the remainder may practically be noted as nitrate. 8 grammes of pure potassium bichromate for every 2 grammes of nitrite taken are dissolved with a little water in a flask fitted with a well-ground stopper; an excess of sulphuric acid is then added, and the flask is placed in a vessel containing a mixture of sodium sulphate and hydrochloric acid. The solution of the nitrite may be placed also in the same freezing bath for a few minutes previously to being poured on the surface of the chromic acid without mixing; the stopper is then inserted, the flask taken out of the freezing-mixture, inverted, and left to regain the ordinary temperature of the room; in the course of half an hour or an hour the flask will contain a mixture of chromic acid and chromic salt, the chromic oxide representing the nitrite in the sample.

In precipitating the chromic oxide a precaution is necessary. If there is any considerable excess of chromic acid left, which is generally the case, when examining commercial samples, the ordinary method of precipitating with ammonia would not do, as a brown precipitate of a chromium peroxide, not decomposable by ammonia, is thrown down, although the substance is instantly decomposed, upon boiling, by a solution of potash into chromic oxide and chromic acid. It is therefore necessary to nearly neutralise with potash, and finish off with a few drops of ammonia, and boil until all trace of the latter substance is gone; but if accidentally too much potash is added, a few drops of ammonium chloride and boiling for a few minutes will rectify the mistake. If the manipulation has been correctly performed, it will be indicated by the colour. The dark brown colour instantly disappears

on boiling, the precipitate taking the bright green of chromic oxide, whilst the solution becomes a bright yellow.

The chromic oxide is washed, but for accurate results it retains the potassium chloride too tenaciously to ignite and weigh directly. It is better to redissolve the washed hydrated chromic oxide in dilute hydrochloric acid, and to reprecipitate with ammonia in the usual manner. This gives the most exact results; but there are quicker methods. Thus, the hydrated chromic oxide might be washed and converted into chromic acid by Chancel's method (by lead peroxide) and estimated volumetrically.

Chromic oxide found $\times 1.854$ = sodium nitrite.

The second process is based upon the first, that both nitrites and nitrates of the alkalies are converted into chlorides upon ignition with ammonium chloride.

Pure sodium nitrite gives 84.78 per cent. of sodium chloride, whilst sodium nitrate only gives 68.82. From these data it is therefore easy to calculate the percentage, as anything under 84.78 indicates the presence of nitrate.

It must be borne in mind that if the specimen contains carbonate, this would give the percentage of nitrite too high. As 100 parts of carbonate would give 110.87 parts of sodium chloride after ignition, therefore it will be necessary to deduct an equivalent quantity of sodium chloride from the results before calculating them. A weighed quantity of the nitrite is intimately mixed with powdered ammonium chloride, and introduced into a platinum crucible; a gentle heat is applied, until the whole of the excess of sal-ammoniac and other gaseous bodies are volatilised. The residue is dissolved in water, and the sodium chloride estimated volumetrically with a silver solution.

After a deduction for any sodium carbonate present, the calculation may be made thus :

$$\frac{(\text{NaCl} - 68.82) + 100}{15.06} = x,$$

x being the percentage of sodium nitrite. The sodium chloride left, minus the percentage of nitrate, divided by the difference, (15.96), will give the percentage of nitrite, or *vice versa* :

$$\frac{(84.78 - \text{NaCl}) + 100}{15.96} = x,$$

x being in this case sodium nitrite; ammonium nitrite in solution is resolved on boiling into nitrogen and water.

(b.) **When Minute Quantities only are Present.**—Nitrites have the property of liberating iodine from an acidified solution of potassium iodide. Dr. Angus Smith asserts that an amount of nitrous acid, so small as 1 in $8\frac{1}{4}$ millions of water, may easily be discovered in this manner. Mr. P. Holland has made use of this qualitative test for the purpose of quantitative estimation, the colouration imparted by the

free iodine being taken as the measure of the nitrous acid present. For a 'colorimetric' standard, solution of iodine in potassium iodide is taken; about 4 grammes is dissolved in excess of iodide, and made up to the volume of a litre. In the next place it is necessary to prepare a pure salt of nitrous acid; for this purpose commercial potassium nitrite is precipitated with silver nitrate, the resultant silver salt washed by decantation, recrystallised, and dried *in vacuo*.

To 0.8276 gramme of the silver salt, dissolved by heat in water, is added a slight excess of pure sodium chloride, and the liquid, when cold, made up to the volume of 1,000 c.c.; therefore 10 c.c. = 1 milligramme of nitrous acid.

The iodine solution is titrated as follows:—A permanganate burette divided in $\frac{1}{10}$ of a c.c., and fitted with a float, is filled with it. Two narrow white glass jars are placed on a white slab; on each is marked the point at which a volume of 200 c.c. of water stands. Into one, A, is put an amount of the standard nitrite equal to 1 milligramme of nitrous acid, together with 6 c.c. of potassium iodide (1 to 10 of water), then distilled water nearly to the mark, and lastly, dilute sulphuric acid. The whole is to be mixed and allowed to stand until the colour is fully developed; when that point is reached, the second jar, containing an amount of potassium iodide, and acid equal to that in A, is filled to within a short distance of the volume mark with water, and placed under the burette; the iodine solution is then cautiously delivered into it, until the depth of colour is judged to be equal in intensity to that in A. The iodine solution should be of such a strength that 10 c.c. have a colouring power equal to that possessed by 1 milligramme of nitrous acid in the presence of potassium iodide in a volume of 200 c.c. of water. It is unadvisable, when making the comparison, to add the standard nitrite from a burette to an acidified solution of potassium iodide, for an obvious reason. It may, however, be suggested that a definite quantity of nitrite should be added, together with iodide, to the water in the jar, and lastly the acid. Such a method is tedious, in that it would be necessary to make several assays before attaining the desired shade.

The following estimations of nitrous acid have been made in this manner:—An amount equal to 1 milligramme was evaporated with a litre of spring water to the volume of 100 c.c., the residue was filtered into the cylinder, and the filter washed; when cold some potassium iodide was added, then distilled water to within $\frac{1}{4}$ inch of the mark, and lastly dilute sulphuric acid. After thoroughly mixing, the contents of the cylinder were left undisturbed, for the colour to become fully developed; when that stage arrived it was found that 11.5 was the number of c.c. of iodine requisite to impart the same colour to an equal volume of water. Ten c.c. only should have been required; the excess, therefore, of 1.5 c.c. is the measure of the nitrous acid in the water employed.

The process is not suitable when the quantity of nitrous acid is

large; whilst it ranges below and up to 1 milligramme concordant results can be obtained.

Some precautions are necessary in certain cases. Sulphuretted hydrogen and sulphides must be removed if present; the former escapes during the evaporation of the water; the latter may be decomposed by a metallic oxide. Organic colouring matter can be precipitated by means of calcium chloride, sodium carbonate, and a few drops of potassium hydrate, as suggested by Dr. Frankland. Kaolin could, perhaps, be employed for the purpose.

For estimating the nitrous acid in the Gay-Lussac column, Kolb gives the following process:—1 gramme of pure dry potassium permanganate corresponds to 0.6 gramme nitrous acid, and converts it into 0.85 gramme anhydrous nitric acid. The permanganate must not be dropped into the acid, but the acid under examination must be dropped into a known volume of permanganate until the latter is decolourised. Cold dilute nitric acid has no action upon permanganate. Kolb operates upon 0.5 gramme of permanganate in solution, and the volume of acid employed to decolourise it shows the amount of nitrous acid contained. To the liquid is now added a known volume of the normal solution of iron, and the whole is boiled to expel hyponitric acid. Dilute with boiled water, stopper the flask, and when completely cool, titrate with normal permanganate. We obtain thus an amount of nitric acid, from which it is necessary to deduct that furnished by the former operation, and which has been calculated into nitric acid. The difference shows the real quantity of nitric acid existing in the volume of liquid used, in the first place, to decolourise the 0.5 gramme of permanganate. Suppose, for example, that it was needful to use 10 c.c. of the sample of acid to decolourise the 0.5 gramme of permanganate. These 10 c.c. contain 0.3 gramme of nitrous acid. If, in the second place, it is found by means of the normal solution of iron that the same 10 c.c. of acid contain 0.572 of nitrous acid, from this quantity we must deduct 0.425, the equivalent in nitric acid of the 0.3 of nitrous acid. There remains 0.147 of nitric acid for the 10 c.c. of acid operated upon, or in 100 parts—

Nitrous acid	.	.	.	3.00
Nitric acid	.	.	.	1.47

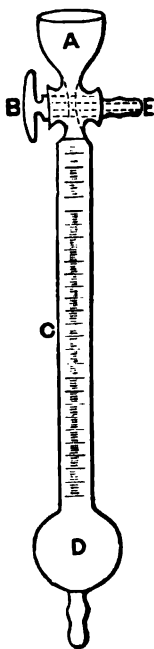
For estimating the nitrogen compounds in the acids from the Gay-Lussac column and the Glover tower, and also in chamber acid, Mr. G. E. Davis remarks that if arsenious acid is present in the vitriol, the process of examination by either the chloride of lime or the permanganate method or the bichromate method would be incorrect, seeing that arsenic acid would be produced from the arsenious compound, and the amount of the deoxidation would be reckoned as nitrous acid.

The methods of oxidation alluded to can only be exact, or approximately so, when the arsenic compounds are in a state of peroxidation, and the vitriol is free from organic matter and iron proto-salts, and

also when the nitrogen oxides are all in the same degree of oxidation, and that degree positively known. It is therefore certain that none of the oxidation methods can be used for estimating with certainty the amount of nitrogen compounds in ordinary pyrites vitriol, and only under certain conditions is it permissible to use an oxidation process for the estimation of the nitrogen compounds in brimstone vitriol.

He proposes the following modification of a process devised by Mr. Walter Crum :—1 c.c. of the vitriol is measured very accurately by means of a fine pipette, and introduced into Frankland's stopcock-tube, standing over mercury. By opening the stopcock the vitriol is allowed to run in, and the cup is washed out with pure strong vitriol which is also run into the tube. The bottom is now closed with the thumb, and the vitriol agitated with the mercury in such a manner that an unbroken column of mercury always remains between the vitriol and the thumb. The reaction is complete in less than 5 minutes, and the tube being graduated, the mercury is levelled, and the volume of gas read off. For technical purposes this volume will be found accurate enough, but in cases where extreme accuracy is required, the tube must be left to itself for several hours, the temperature and pressure noted, and the necessary corrections made.

FIG. 8.



The mercury reduces the whole of the nitrogen oxides to nitric oxide, and the presence of any other compound found in vitriol has no influence on this test. The only precaution to be taken is to have the vitriol in the tube strong enough.

For working out this process Mr. Davis has devised a convenient and economical mercurial trough, which is supplied by Messrs. Mottershead of Manchester.

Another apparatus for the purpose, known as Tennant's nitrometer, is here figured :—B is a three-way stopcock, having a passage between the tube c and the cup A, and between c and the waste-pipe E. G is a tube graduated to 80 c.c. in fifths. A piece of caoutchouc tubing is fixed to the outlet of the globe D, and carried to a bottle or reservoir for mercury, from whence the graduated tube may be filled.

A measured quantity of the acid to be tested is then introduced into the cup A, and, by lowering the mercury reservoir and opening the stopcock, allowed to pass into the graduated tube. The stopcock is then closed, and the column of acid vigorously shaken till its reaction on the mercury is completed.

CHAPTER XII.

IODINE, BROMINE, CHLORINE, FLUORINE (CYANOGEN).

IODINE.

Purification of Iodine by Sublimation.

IODINE should not leave any residue when exposed to a high temperature. Impure iodine may be purified by sublimation in the following manner:—Place it in a large watch-glass resting on a plain glass plate, and heat it on a sand-bath to 107° C. (the melting-point of iodine); a well-cleaned beaker is inverted over the watch-glass, and in this the iodine condenses.

Assay of Commercial Iodine.

The methods generally adopted, based on the well-known reactions of sulphurous acid or sodium thiosulphate, yield excellent results in experienced hands, but are attended with many sources of error owing to the rapid alterations in the standard solutions. Mohr's method, based on the use of sodium arsenite, is much more accurate, and with the modifications introduced by M. A. Bobierre, leaves little to be desired on the score of accuracy or speed.

Make a concentrated solution of potassium iodide, which should remain unchanged for a certain series of experiments; this is to dissolve the iodine which is to be tested. The standard solution of sodium arsenite is obtained by dissolving 4.95 grammes of arsenious acid with 14.5 grammes of crystallised sodium carbonate, and diluting the aqueous liquid to 1 litre. This solution should decolourise an iodised liquid containing 12.688 grammes of iodine per litre. But supposing that the arsenious liquid may not have this reducing power, the test will be none the less exact, as at the time of performing it the relation of a given weight of pure iodine to the arsenite will also be estimated. A somewhat concentrated solution of sodium bicarbonate is also to be prepared.

The analysis is best effected in a small stoppered flask. Into this are put 10 c.c. of the sodium arsenite, to which must be added 5 c.c. of alkaline bicarbonate solution; the whole then receives a further addition of about 4 c.c. of perfectly colourless benzol.

Weigh a certain quantity of pure iodine between two watch-glasses;

dissolve this in the concentrated solution of potassium iodide prepared beforehand, and which must be of the same strength in all the various estimations which may be made; with this coloured solution fill a flask containing 100 c.c., shake it, and pour the contents into a graduated burette.

On allowing the iodised solution to fall into the arsenite drop by drop, and stirring it quickly, the brown colour will be seen to disappear instantaneously; but scarcely will all the arsenite have been changed to arseniate, when the addition of iodine will produce a double reaction; in the first place, the benzol will turn red; secondly, the aqueous liquid, which was perfectly colourless at the beginning of the operation, assumes a very sensibly yellowish tinge. The significant character of this is the more surprising when we remember the very small quantity of iodine which causes it.

A second experiment is now to be performed upon the iodine to be estimated, and the same weight being used, its standard is at once shown, since the volume of solution requisite to destroy the alkaline arsenite is in inverse proportion to the quantity of real iodine to be estimated.

Detection of Minute Quantities of Iodine.

1. Make a mixture of water, 100 grammes; starch, 1 gramme; potassium nitrite, 1 gramme: boil this for 5 minutes; it will then keep for years without deterioration. When required for use, take 10 c.c., and add to it one drop of hydrochloric acid. Take a piece as large as a pin's head of the dry salt to be tested for iodine, place it in a clean porcelain capsule, and add a drop of the test fluid. When no iodine is present, no colouration ensues; but the least trace of iodine gives rise to the formation of a well-defined blue colour.

2. Carey Lea makes use of the oxidising properties of chromic acid to liberate iodine from its hydrogen and metallic combinations and thereby bring about the starch reaction.

If, for example, we take an extremely dilute solution of potassium iodide, such that the addition of nitric acid and starch produces no perceptible effect, the further addition of a single drop of very dilute solution of potassium bichromate will instantly bring about the characteristic reaction. When hydrochloric acid is substituted for nitric, the effect of the bichromate is still more marked. The test has, then, the full delicacy at least of the chlorine test, with this great advantage, that an excess of the reagent does not prevent the reaction. As to the delicacy of this test, the following observations have been made:—With solutions of potassium iodide up to $\frac{1}{100000}$ the precipitate is abundant, becoming less blue and more tawny as the dilution increases. Beyond this point the distinctness rapidly falls off. The indications are observable at $\frac{1}{100000}$. With a solution of $\frac{1}{300000}$ it

is doubtful whether any effect is evident. The experiment can be made in two ways, according to the result desired.

In employing the reagent in the search for iodine, add the starch to the liquid to be tested, stir it up, add a drop of dilute solution of potassium bichromate, enough to communicate a pale yellow colour, and finally add a few drops of hydrochloric acid. The test is then the production of the characteristic precipitate, or in case of great dilution, approaching to a half-millionth, merely the tawny shade given to the solution.

If a very great excess of acid is used, and too much bichromate taken, the starch may be made to reduce the bichromate. Even this, however, cannot deceive, for a bluish-green solution is thereby produced, whereas the indications of iodide are in the order of their strength—blue precipitate, tawny precipitate, tawny solution. Unless in the case of very exceptional dilution above spoken of, a well-marked blue precipitate is always obtained.

8. The method of estimating iodine by the thiosulphate process is best conducted as follows :—

Prepare a normal standard solution containing, for each litre of water, about 40 grammes of sodium thiosulphate, so that 50 c.c. of this solution will completely decolourise 1 gramme of iodine.

Then take 10 c.c. of the iodised liquid to be tested, diluted with water if it be very concentrated or rich in iodine; then add carefully, after it has been acidulated with hydrochloric acid, some drops of hyponitric acid. When it becomes yellow, shake it with benzol or petroleum, which will immediately turn rose or violet. Separate the iodised benzol from the acid liquid, and repeat the operation until the solvent liquid ceases to become coloured.

Collect the iodised benzol resulting from these treatments, and wash it with distilled water, which will remove all traces of chlorated or bromated compounds without removing any appreciable quantity of iodine. Then, with constant stirring, add, by means of a burette graduated to tenths of a c.c., the standard thiosulphate liquid until all colour is destroyed; each cubic half-centimetre of the normal liquid will correspond to one centigramme of iodine contained in the liquids assayed.

It is always necessary to desulphurise solutions containing sulphides, sulphites, or thiosulphates, by boiling them with nitric, sulphuric, or hydrochloric acid.

To ascertain the purity of commercial iodines, dissolve about 50 centigrammes in diluted alcohol, and operate as above.

To ascertain the quantity of iodine in dry or wet sea plants, cut them into small pieces; place them in a porcelain capsule and cover them with alcohol; set fire to the alcohol, carefully stir the mass with a glass rod, and the carbon will be obtained without loss of iodine; then well wash the latter, and act on the solution as above described.

Detection of small quantities of Iodine in Sea-water, etc.

The liquid to be tested is placed in a test-tube along with carbon disulphide, and a very few drops of dilute sulphuric acid. Hereupon the vapour of red fuming nitric acid is allowed to fall for a moment into the tube. After strong agitation, the carbon sulphide is coloured rose colour if the slightest trace of iodine is present.

M. A. Chatin points out certain causes of failure in the detection of minute quantities of iodine in potable waters, etc. It is needful to precipitate the soluble calcium and magnesium salts with an excess of pure potassium carbonate. The iodine being thus fixed will be found in the residue after evaporation, which is slightly ignited to destroy organic matter. The liquid must be separated by decantation from the earthy carbonates, which will be deposited during the first quarter of the evaporation. Towards the end of this process the heat must be diminished to avoid any loss of the soluble residue by spirting. This last point is important, as the iodide is among the last drops evaporated. The excess of carbonate remaining after the precipitation of the calcium-magnesium salts should be the larger the more organic matter is present. We may ascertain that this excess has been sufficient, either by the residue appearing colourless after calcination, or by the circumstance that although coloured it forms a paste if treated with alcohol at 90 per cent. If the alkaline carbonate has been insufficient, the residue will be divided in the alcohol, like a powder; the iodine then escapes in great part or entirely during calcination. The alkaline residue left on the evaporation of the water must be three times treated with alcohol, and the solutions are mixed together in a capsule capable of holding at least four times the quantity. Before proceeding to evaporate, which must be done at a low temperature, the alcohol is mixed with about half its volume of pure distilled water. The water should have been distilled after an admixture with potassium carbonate. Frequent agitation is useful. Slight calcination is again needed to destroy a certain quantity of organic matter which has escaped the former ignition, and the presence of which would mask the character of traces of iodine. The residue at the bottom of the capsule should be colourless and scarcely perceptible. If it is very appreciable in quantity too much alkaline salt is present, and it must be redissolved in alcohol. The last condition is that this residue must be dissolved in a minimum of water, 2 drops, or even a single drop, which must be led over the bottom of the capsule with a glass rod, so as to dissolve all the iodide present. With the end of the stirrer this liquid is divided into three or four portions, one of them—which will give the most distinct reaction—being left in the bottom of the capsule, the others being placed on fragments of porcelain. One of these little drops is mixed with palladium chloride; the others, having first received a trace of recently made starch-paste, are carefully touched, the one with nitric acid,

the other with commercial sulphuric acid ; chlorine water only gives the blue colouration if the quantities are more considerable. A common cause of failure is the use of chlorine water, and of too dilute solutions. Earths, ores, metals, sulphur, etc., are first finely divided, and then boiled in a solution of potassium carbonate, which is then treated as above. It is well to make blank experiments in researches of this kind. M. Sergius Kern recommends that palladium salts should be very carefully used in analysis for the detection of iodine, because in presence of potassium-ferrocyanide or potassium-ferricyanide the iodine is not detected, and cannot be separated from bromine or chlorine by palladium chloride. So as gold salts also give, with potassium ferrocyanide, a green colouration, this reagent may give faulty results, as it was remarked that palladium salts give the same colouration.

If palladium salts are used as a reagent for iodine, the preliminary analysis must be very carefully executed, in order to be quite convinced of the absence of double potassium ferrocyanides and other cyanides. In presence of alkaline sulphocyanides iodine is not precipitated by palladium nitrate or chloride.

Estimation of Iodine in Organic Liquids.

1. There are met with in commerce mother-liquors which are utilised for the manufacture of iodine, and which contain, besides this metalloid, sensible quantities of alkaline arseniates and arsenites, as well as organic matter. These liquids occur in the manufacture of aniline colours, and their value depends upon the amount of iodine they contain. The following is the best process to adopt for estimating this :— 10 grammes of liquid are treated with 2 grammes of concentrated solution of caustic potash ; the mixture is then evaporated to dryness under a chimney with a good draft, or in the open air, on account of the cacodylic products occasionally evolved ; it is ultimately ignited. The aqueous solution of the residue is diluted with water and treated with a mixture of sulphuric and hyponitric acids. The iodine is separated by agitating with carbon disulphide, and this carbon disulphide solution agitated with water until the washings no longer affect litmus-paper ; when this is attained, a titration of the iodine present is made with sodium thiosulphate or arsenite.

2. To estimate the iodine contained in organic hydriodates, M. Kraut proposes that their solution be digested for some time with a known weight of recently-precipitated silver chloride ; the chlorine is replaced by iodine, and from the increase in weight of the silver chloride the amount of iodine may be calculated. This method has the advantage of not altering the substance beyond removing its iodine, which is replaced by chlorine.

Reinige describes a very interesting method for the estimation of iodine, viz. by means of potassium permanganate. 2 equivalents of the latter and 1 equivalent of potassium iodide produce 1 of

potassium iodate, 2 of free potash, and 4 of manganese peroxide. The decomposition is assisted by boiling the solution, and if the latter is very dilute, a little potassium carbonate is added to induce the commencement of the reaction. As bromine and chlorine are not in the least acted upon under the same circumstances, this reaction is, perhaps, the most convenient for the estimation of iodine. The latter must be combined with potassium, and the solution rendered nearly neutral, but still slightly alkaline. It is heated till it boils gently, and a solution of 2.5 grammes potassium permanganate in 497.5 grammes water is gradually added, removing the beaker from the lamp each time for a few moments, to allow the precipitated peroxide to deposit, but heating it again to the boiling-point before adding another portion of permanganate. When the solution, after the precipitate has subsided, shows a distinctly reddish tint, all potassium iodide is decomposed. The small excess of permanganate is estimated by sodium thiosulphate, and the remainder shows exactly 2 milligrammes of iodine for each c.c. of the permanganate solution used. The results are very accurate.

BROMINE.

Detection of Bromine.

The best solvent for bromine just displaced by chlorine is carbon disulphide, a substance long used in France for detecting iodine. M. Fresenius, who has verified this fact with his usual care, insists on the necessity of avoiding excess of chlorine, and of employing carbon disulphide free from sulphurous and sulphuric acid.

His preference for carbon disulphide over ether and chloroform is founded on a series of direct experiments with standard solutions containing various proportions of bromides. Solutions containing only $\frac{1}{10000}$ of bromine in the state of potassium bromide, when treated with the requisite quantity of chlorine, do not communicate the least colour to ether or chloroform, while carbon disulphide acquires a decided yellow tint. Moreover, being heavier than water, it sinks to the bottom of the liquid with the bromine it has dissolved, and there remains.

If the bromide is accompanied by an iodide, the iodine must be previously eliminated by adding a little hyponitric acid and a drop of carbon disulphide, which takes away the displaced iodine. After this the separation of the bromide may be proceeded with.

Detection of Bromides in Potassium Iodide.

Dr. E. van Melckebeke finds that if to a saturated solution of potassium bromide a small quantity of pure iodide is added it will completely dissolve, but if the iodide is contaminated with potassium bromide this impurity will remain undissolved; 100 parts of water

(distilled), at 16°, dissolves 140·1 parts of potassium iodide, and the same quantity of water, at the same temperature, dissolves 68·89 of potassium bromide: 100 parts of water saturated with bromide dissolve only 18·15 parts of potassium iodide, and if more of that salt be added bromide is precipitated. As the solution of the salts in water causes a very sensible lowering of temperature, for testing, the author recommends to dissolve pure potassium bromide in warm water, to let this solution cool, and decant from the crystalline deposit. To 10 c.c. of this solution 10 drops of water are added in a test-tube, and afterwards in small quantities, and, constantly shaking, 1 gramme of the suspected iodide in coarse powder; if free from bromide it will dissolve almost instantly, while if bromide is present it will remain undissolved.

Solution of Bromine as a Reagent.

M. L. de Koninck has for three years successfully used the solution of bromine in a 10 per cent. solution of potassium bromide. The author recommends it for the precipitation of manganese from an acetic solution, for the conversion of arsenious into arsenic acid, and for the detection of nickel in presence of cobalt in a potassium cyanide solution.

Detection of Chlorine, Iodine, and Bromine in Organic Matter.

C. Neubauer introduces a little copper oxide into the loop of a platinum wire, and heats till it adheres. It is then dipped into the substance, or a little of the latter if dry is sprinkled upon it. The loop is then brought into the flame of a gas-burner moderately opened, near the lower and inner margin of the flame. The carbon burns first, and the flame becomes luminous, followed by the characteristic blue or green colour.

Estimation of Bromine and Iodine in the Presence of Chlorine.

1. This process is of special use for the assay of mother-liquors from saltpetre and kelp. A measured quantity of the liquor is introduced into a long tube with 20 alkalimeter measures of carbon disulphide; and nitrous sulphuric acid (prepared by passing nitrous acid through sulphuric acid) is added, drop by drop, till iodine ceases to be liberated. The tube is inverted several times after the addition of each drop of acid, in order that the iodine may at once be dissolved by the carbon disulphide, to which it gives a violet colour, varying in intensity with the amount of iodine in solution. The quantity of the iodine is estimated by comparing the degree of the colour with that which results when a standard solution of potassium iodide is used in the same way. The delicacy of the reaction is such that 0·01 gramme will communicate a distinct rose tint to the carbon disulphide. When

the amount of iodine exceeds 0.2 gramme of iodine in the quantity operated on, a difficulty occurs, as the violet colour becomes so deep that the various shades cannot be distinguished with accuracy. When all the iodine is separated by the carbon disulphide, the solution containing the bromine is introduced into another tube, and the bromine is liberated by chlorine water in the usual way, and taken up by a fresh quantity of carbon disulphide. In this case, an orange colour is the result, and the amount of bromine may be estimated by comparing the colour with that resulting when a solution of potassium bromide is used of known strength.

2. Colour tests being always liable to much uncertainty in their indications if any great accuracy is desired, the following process may be found preferable. It is devised by Mr. Tatlock, and is based upon the wide difference between the equivalents of iodine, bromine, and chlorine. The mode of procedure depends upon the displacement of iodine by bromine, and of iodine and bromine by chlorine.

The solution containing the iodide, bromide, and chloride, preferably in combination with an alkali metal, is divided into 3 equal portions, or, at any rate, 3 equal portions of it are drawn off. To the one, solution of silver nitrate is added in excess, to precipitate the whole of the iodine, bromine, and chlorine. The fluid is then feebly acidified with pure nitric acid, warmed, and agitated till the precipitate settles. This is collected on a small weighed filter, washed with hot water, dried as far as possible at 100° C., removed from the filter, dried perfectly by heating to incipient fusion, and weighed, the weight of the small portion adhering to the filter being added, and the weight of the whole noted as—



Another portion of the solution is transferred to a small basin, and a quantity of pure bromine water added. The mixture is then carefully evaporated on an open water-bath, more bromine water being added from time to time, till the escaping vapours no longer turn starch-paper blue on a fresh addition—showing that all the liberated iodine has escaped. To ensure excess, a little more bromine water is added, and the solution evaporated to complete dryness. The dry residue is then drenched with water, and the result heated till again dry; this operation is repeated two or three times, to ensure the complete expulsion of any hydrobromic acid that may have been present in the bromine water. The residue, which now consists solely of alkaline bromide and chloride, is dissolved in water, silver nitrate added in excess, the solution acidified, and the precipitate collected and weighed in the usual way. It is noted as—



The last portion of the solution is brought into a small basin, and a quantity of strong chlorine water added, to effect the liberation of

the iodine and bromine. The mixture is then evaporated till all colour is gone, and some more chlorine water added. If the solution remains colourless, the whole of the iodine and bromine has been expelled, and the alkali metal will exist entirely as chloride. The solution is then brought completely to dryness, after which it is evaporated with a few drops of water two or three times, to expel any hydrochloric or hydrobromic acid. The dry residue is dissolved in water, the solution acidified with pure nitric acid, silver nitrate added in excess as before, and the silver chloride collected as usual. Its weight is noted as—



It is obvious that we have now data from which we can calculate the amounts of iodine, bromine, and chlorine present; for, as the equivalent of bromine is less than that of iodine, in the proportion of 80 to 127, the second precipitate, in which the iodine is replaced by bromine, must weigh proportionately less than the first; and, as the equivalent of chlorine is less than that of either iodine or bromine, in the ratio of 35.5 to 127 in the one case, and to 80 in the other, the last precipitate must weigh still less than the second, and we can thus, from the observed differences, deduce the exact quantities of the three elements present.

Example :—

1. $\text{AgI} + \text{AgBr} + \text{AgCl}$ weighed 15.57
2. $\text{AgBr} + \text{AgBr} + \text{AgCl}$ „ 14.69
3. $\text{AgCl} + \text{AgCl} + \text{AgCl}$ „ 12.20

Then—

I.		II.		Observed difference.	
15.57	—	14.69	=	0.88	
Loss for 1 equiv. I.		Observed loss.		1 equiv. I.	I present.
47	:	0.88	::	127	: 2.378

I.		III.		Observed difference.	
15.57	—	12.20	=	3.37	

But, as a portion of this loss is caused by the replacement of iodine by chlorine, namely—

Equiv. of I.	Loss in replacing 1 equiv. I. by Cl.		I found.	Loss accounted for by I present.	
127	:	91.5	::	2.378	: 1.713
Observed loss.		Loss accounted for by I present.		Difference for Br.	
3.37	—	1.713	=	1.657	

Loss for 1 equiv. Br.	Observed loss on account of Br.		1 equiv. Br.	Br found.	
44.5	:	1.657	::	80	: 2.978

Then, as the proportion of iodine and bromine are already known, it will be an easy matter to calculate them to iodide and silver bromide,

and deduct their weight from precipitate 1, calculating the remainder (silver chloride) to chlorine, thus :—

	I.	:	AgI.	::	I present.	:	AgI.
	127	:	235	::	2·378	:	4·400
And—							
	Br.	:	AgBr.	::	Br present.	:	AgBr.
	80	:	188	::	2·978	:	6·998
Then—							
	AgI	4·400
	AgBr	6·998
							<hr/> 11·398

Then—

$$15·57 - 11·398 = 4·172$$

Then—

AgCl.	:	Cl.	::	AgCl.	:	Cl.
143·5	:	35·5	::	4·172	:	1·032

There were, therefore, present in the solution—

Iodine	2·378
Bromine	2·978
Chlorine	1·032

The bromine water may be easily obtained free from chlorine by distilling potassium bromide in solution with less potassium bichromate than is necessary to expel the whole of the bromine, using, of course, a little hydrochloric acid.

Application of the Foregoing Method to the Analysis of Kelp.—It is quite obvious that this process cannot be directly applied to substances containing iodine, bromine, and chlorine, in very different proportions, and consequently it cannot be used for the estimation of these elements in kelp immediately. The following method of treatment will be found to equalise as nearly as necessary the proportions of the three :—

2,000 grammes of the kelp are digested in hot water, the solution allowed to settle, and the clear liquor filtered. The residue is boiled two or three times with water, the fluid being filtered in each case, and the residue finally brought on a filter and washed with boiling water. The filtrates and washings are neutralised as nearly as possible with hydrochloric acid, and chlorine gas passed into the solution till the latter becomes of a distinct orange colour, due to the liberation of iodine and bromine.

The fluid is then shaken up with about $\frac{1}{4}$ of its bulk of carbon disulphide, which takes up the liberated iodine and bromine, and carries them in solution to the bottom of the vessel, provided the sp. gr. of the kelp solution be not higher than that of the carbon disulphide. When this is not the case, the solution of kelp may be diluted till the carbon disulphide sinks.

The bottom fluid, containing the iodine and bromine, is then drawn off by a fine syphon, and shaken up with an equal volume of water and some zinc filings. The solution is soon decolourised, on account

of the formation of zinc iodide and zinc bromide, which pass into the water; and we have thus an aqueous solution of the two latter salts above, and colourless carbon disulphide at the bottom. The latter is drawn off by a syphon, and restored to the kelp solution, to which some more chlorine water is added; and, if a further quantity of iodine and bromine be liberated, the above operations are repeated till the liquor is quite exhausted.

It only now remains to evaporate the solution of zinc salts, divide into 8 equal portions, and determine iodine, bromine, and chlorine, as before described.

Detection of Bromides in the Presence of Chlorides.

When gold chloride is added to a faintly acid solution of an alkaline bromide, a colouration is produced ranging from dark orange red to light straw colour according to the strength of the solution. Iodides must not be present; chlorides, however, do not interfere. The best mode of proceeding is as follows:—Remove the iodides, if present, by means of palladium, and after getting rid of excess of palladium by sulphuretted hydrogen, concentrate the solution to about 25 c.c. Select two test-tubes of the same size and shape and colour of glass; into one pour the solution suspected to contain bromine, and into the other pour pure water containing a trace of potassium chloride. Add to each tube one drop of hydrochloric acid, and one drop of gold chloride solution. On now comparing the two tubes, particularly in the direction of the long axes, a yellow colour will be observed in the tube containing the bromide, which will be rendered very manifest by comparison with the other tube.

The mixed chloride and bromide should be brought to the state of alkaline salts if necessary, by precipitating with silver nitrate, thoroughly washing and fusing with *potassium* carbonate. If sodium carbonate is used for this purpose the subsequent reaction with the gold test is not so decided.

Detection of Chloride in Potassium Bromide.

The bromide to be examined is first tested for iodine. For this purpose a small quantity of the salt is dissolved in water in a test-tube, and an equal volume of carbon disulphide added. Upon the addition of a few drops of bromine water, the carbon disulphide becomes coloured violet, under the influence of iodine, if this be present. When the test shows the presence of iodine, it is necessary to remove the whole of this element from the sample. This is effected by dissolving about 10 grammes of the salt in distilled water, adding bromine water until violet vapours are no longer visible upon boiling, and then testing for iodine in the manner first described. Afterwards the solution is evaporated to dryness to remove the excess of bromine,

and thus is obtained a potassium bromide free from iodide, but which may contain chloride.

The remainder of the process depends upon the fact that a given weight of potassium chloride requires, for complete precipitation, a much greater amount of a standard solution of silver nitrate than the same weight of potassium bromide. While the bromide for the complete precipitation of 1 gramme requires 1.428 gramme of silver nitrate, 1 gramme of the chloride requires 2.278 grammes. A standard solution of silver nitrate is first prepared by dissolving 10 grammes of the pure salt in a litre of water, each $\frac{1}{10}$ c.c. corresponding to 1 milligramme of silver nitrate; 1 gramme of the bromide to be examined, freed as above from iodine, is dissolved in 100 c.c. of distilled water; 10 c.c. of this solution, representing 0.1 gramme of potassium bromide, would require, if pure, 14.2 c.c. of the silver solution; potassium chloride would require 22.7 c.c.

M. Baudrimont has proposed a method of making the final reaction more delicate, by adding a few drops of solution of potassium chromate to the bromide examined; the silver nitrate added at first combines with the whole of the bromine and chlorine in preference, and the complete precipitation is marked by the production of the red precipitate of silver chromate. It is obvious that the bromide contains more or less chloride, according as the number of burette divisions (divided into $\frac{1}{10}$ c.c.) of the silver salt required exceeds 142. With a salt containing $\frac{1}{10}$ of its weight of potassium chloride 151 divisions are required, and with a mixture of equal weights of chloride and bromide, 185.

The same method may be employed to recognise the degree of purity of several compounds. Operating as before—that is to say, dissolving 1 gramme of the material to be examined in 100 c.c. of distilled water, and taking 10 c.c. of the solution—the following numbers of $\frac{1}{10}$ c.c. divisions required will show the purity for at least a considerable number of salts:—102 for pure potassium iodide, 257 for potassium cyanide, 246 for dry potassium carbonate, 290 for sodium chloride, 119 for sodium carbonate + 10 equivalents of water, 47 for sodium phosphate + 24 equivalents of water, and 54 for sodium arseniate + 14 equivalents of water.

Detection of Iodine in Potassium Bromide.

When potassium bromide is suspected to be adulterated, or mixed with potassium iodide, place a few grains of the salt in question on paper previously impregnated with starch-paste, moisten it, and admit a small quantity of chlorine gas, whereby the iodine is set free and the paper coloured blue.

A better test is the use of bromine water added to the salt after it has been placed in benzol; if the latter becomes red-coloured, iodine is present.

CHLORINE.

Estimation of Chlorine with the aid of Gooch's Method of Filtration.

Mr. David Lindo remarks that it is generally considered that chlorine can be estimated with great exactness by the gravimetric method.

Silver chloride being slightly soluble in water, especially in hot water, a small minus error may occur if the latter is employed to wash with, but this can be prevented by adding a little silver nitrate to the water, as recommended by J. P. Cooke.¹

On the other hand, the precipitate retains occluded matters with great force. Error from not completely removing these often more than compensates for slight loss occasioned by the use of hot water alone, or merely acidulated with nitric acid, or by the manipulations necessary when paper filters are employed.

According to Fresenius,² we can, with great care, always obtain by this method 99.9 to 100.1 for 100 parts of chlorine taken. I presume Fresenius means when using paper filters, in which case the time required to make an estimate is generally six hours.

The limits of error here laid down are often reached, according to my experience, when paper filters are employed, and no silver nitrate added to the wash water.

Though sufficiently near for most purposes, greater accuracy in chlorine estimates may sometimes be desired. By adopting Gooch's method of filtration and Cooke's suggestion, with a few other simple precautions, a much higher degree of accuracy can be attained with less manipulation and expenditure of time than by the usual method.

Method:—Weigh the solution in a light glass stoppered bottle, and turn it into a deep porcelain capsule, about $4\frac{1}{2}$ ounces capacity, provided with a well-formed lip and handle. Rinse the bottle with 25 c.c. distilled water. Add solution of silver nitrate in about the proportion of 25 c.c. to 0.5 gramme potassium chloride, and 2 c.c. pure nitric acid, sp. gr. 1.2. Heat to boiling-point, and keep at this temperature for some minutes without allowing violent ebullition, and with constant stirring, until the precipitate assumes the granular form. Allow to cool somewhat, and then pass the fluid through the asbestos. Wash the precipitate by decantation with 200 c.c. of very hot water, to which has been added 8 c.c. nitric acid and 2 c.c. dilute solution of silver nitrate containing 1 gramme of the salt in 100 c.c. of water. The washing by decantation is performed by adding the hot mixture in small quantities at a time, and beating up the precipitate well with a thin glass rod after each addition. The pump is kept in action all

¹ *Chemical News*, vol. xlv., p. 235.

² *Quantitative Analysis*, Seventh Edition, p. 170.

the time, but to keep out dust during the washing the cover is only removed from the crucible when the fluid is to be added.

Put the capsule and precipitate aside, return the washings once through the asbestos so as to obtain them quite clear, remove them from the filter, and set aside to recover excess of silver. Rinse the receiver and complete the washing of the precipitate with about 200 c.c. of cold water. Half of this is used to wash by decantation, and the remainder to transfer the precipitate to the crucible with the aid of a trimmed feather. Finish washing in the crucible, the lumps of silver chloride being broken down with the glass rod. Remove the second filtrate from the receiver, and pass about 20 c.c. of alcohol at 98 per cent. through the precipitate. Dry at 140° to 150° . Exposure for half-an-hour is found more than sufficient, at this temperature, to dry the precipitate thoroughly.

In the volumetric estimation of chlorine, with a standard solution of silver and potassium chromate as an indicator, Prof. A. R. Leeds points out that the chromate employed is more or less contaminated with alkaline chlorides. Hence it is necessary to estimate the number of tenths of a c.c. of the silver solution which correspond to the number of drops used of the particular chromate solution.

Detection and Estimation of Chlorine in presence of Bromine and Iodine.

G. Vortmann has discovered a method by means of which even small quantities of chlorine along with the other halogens can be easily and quickly detected. It depends on the different behaviour of the chlorides, bromides, and iodides with manganese and lead peroxides in presence of acetic acid.

Iodides are partially decomposed by the above-mentioned peroxides, even in neutral solutions, and if they are boiled with the addition of acetic acid the iodine is completely eliminated. Lead peroxide oxidises a part of the iodine to iodic acid, but with manganese peroxide no iodic acid is formed.

In a neutral solution bromides are not decomposed either by manganese or lead peroxide. In an acetic solution the lead peroxide only acts; bromine escapes; but bromic acid is formed only if bromides are present in considerable quantities. Manganese peroxide has no action in the acetic solution, even on prolonged heating.

Chlorides are not attacked by either of the peroxides in presence of acetic acid. In testing for chlorides in presence of bromides or iodides it is sufficient to boil the substance in an acetic solution with lead peroxide till the liquid on settling is colourless and has not the slightest odour of bromine or iodine. The bromine and a part of the iodine escape as such; the remainder of the iodine remains as lead iodate along with the excess of the lead peroxide. On filtering and washing the precipitate, all the chlorine is found in the filtrate free

from bromine and iodine. In this manner the chlorine may be estimated quantitatively. If the quantity of chlorine accompanying the iodine is considerable, manganese peroxide is preferable to lead peroxide, as otherwise the liquid must be largely diluted with water to prevent lead chloride from depositing. In estimating large quantities of chlorine in presence of bromine, it is well to add along with the lead peroxide some potassium sulphate so that all the chlorine may be found in the filtrate combined with potassium.

In order to expel the liberated bromine and iodine more rapidly a moderate current of air may be passed through the solution on the water-bath.

Detection and Estimation of Iodine in presence of Bromine and Chlorine.

E. Donath remarks that whilst potassium bichromate occasions in solutions of potassium iodide no separation of iodine, this result is at once produced by chromic acid. An estimation of the liberated iodine is not possible on account of the action of the excess of chromic acid upon sodium thiosulphate. The iodide of starch is precipitated by solutions of chromic acid as an almost black precipitate. Hence, starch-paste cannot serve as an indicator. The iodine is therefore distilled off, and is estimated in the distillate by means of sodium thiosulphate. The alkaline bromides and chlorides are not decomposed by concentrated solutions of chromic acid at common temperatures, and the chlorides not even on boiling. Dilute solutions of chromic acid decompose the bromides only to a very small extent at the boiling heat, but the proportion increases with increasing concentration. The method is therefore suitable for accurate estimations of iodine in presence of chlorine, but not when it occurs along with bromine. The solution of chromic acid employed contains from $2\frac{1}{2}$ to 3 per cent., and is freed from traces of sulphuric acid by boiling with pure barium chromate.

Estimation of Chlorine in Bleaching Powder.

(a) The commercial estimation of bleaching powder only extends to the estimation of the hypochlorite contained therein; the result being, however, calculated as so much per cent. of 'available chlorine.' Of the numerous methods proposed for the estimation of the hypochlorite, the one usually employed in the trade is that depending on the amount of ferrous salt oxidised by a given weight of bleaching powder. It frequently happens, however, that instead of a perfectly pure ferrous salt (such as the ammoniosulphate precipitated by alcohol), the ordinary iron protosulphate of the druggists is used, discoloured crystals being of course rejected. This substance is, however, rarely pure, and hence errors are frequently introduced, less chlorine being required to peroxidise a given weight of impure than of

pure substance. Again, some analysts neglect to add an acid to the ferrous solution used, and hence the precipitated ferric hydrate is liable to carry down perceptible quantities of ferrous hydrate, again making the apparent amount of chlorine required less than that really requisite. When acid is added, an error is liable to be introduced by the peroxidation of part of the iron by chlorine compounds derived from chlorate that may be present. Direct experiments have shown that acid ferrous solutions are perceptibly oxidised by the presence of chlorate in small quantities in the course of a very few minutes, even at the ordinary temperature, although the peroxidation due to the whole of the chlorate is not manifest until after standing some time at $20^{\circ}\text{C}.$, or till after heating to ebullition. Lastly, the equivalent of chlorine is frequently taken to be 86 instead of 85.46 (Stas). All these sources of error tend to make the percentage of chlorine found higher than that really present; accordingly it frequently happens that analyses of the same sample by different analysts differ by 1, 2, or 3 per cent. of available chlorine. This error becomes of serious importance, it frequently happening that the analysts employed by the seller and purchaser differ in their reports, thus causing much annoyance, and possibly the rejection of the goods as not being of contract strength.

As regards the error introduced by the presence of chlorate in the sample analysed, Dr. C. R. A. Wright has made many careful experiments on the subject, which have yielded the following results:—

1. Acid ferrous solutions are peroxidised by addition of a chlorate, at a rate depending on the strength of the solutions, the amount of free acid, and the temperature, the reaction taking place completely after heating to ebullition for a minute, and almost as completely after standing for upwards of half an hour at $20^{\circ}\text{C}.$, time being, however, required for any temperature short of ebullition.

2. Acid solutions of arsenious acid, where a large excess of free acid is present, are scarcely affected by chlorate at $20^{\circ}\text{C}.$ until after standing some hours; the reaction ensues completely on heating to ebullition for a minute, and completely in a few minutes' heating on a water-bath.

3. Alkaline solutions of arsenious acid (containing sodium carbonate and free carbonic acid) are wholly unaffected by chlorate, either cold or boiling, even after several hours.

4. Acid solutions of potassium iodide (free from iodate). Iodine begins to separate even at $20^{\circ}\text{C}.$ in a very few moments on addition of very little chlorate, and after some time much separates. Heated to 100° on the water-bath, the whole of the chlorate becomes completely decomposed, after five minutes, in presence of sufficient free acid.

5. Alkaline solutions of potassium iodide are unaffected by chlorates even on long standing or long boiling.

Where the hypochlorite contained in a sample of bleaching powder, which may also contain chlorate, is to be estimated, the only safe and

convenient method is that of Penot, i.e. by the use of an alkaline solution of arsenious acid. When the chlorate likewise is to be estimated, it may be expeditiously done by heating the sample with a known quantity of the same arsenite solution, and addition of hydrochloric acid; from the difference between the quantities of arsenite peroxidised in the two instances the chlorate is readily known. Dr. Wright has found the bleaching powder of commerce to contain several per cent. of calcium chlorate, even when newly made; in older samples the chlorate has been occasionally found to represent as much as 10 per cent. of available chlorine, or fully $\frac{1}{4}$ of the amount originally present; thus indicating over-heating either in the process of manufacture or subsequently.

(b) 2 grammes of the bleaching powder to be tested are well mixed with water, and the fluid so obtained mixed with a solution of iron protochloride freshly made by dissolving 0.6 gramme of pure iron wire in pure hydrochloric acid. Pure hydrochloric acid in excess is next added, and the fluid boiled in a flask, after previous addition of a piece of rather thick, perfectly clean, and polished sheet copper, of a weight of about 4 grammes. The boiling is continued until the colour of the fluid, at first darkish, has become bright green; the copper is then removed from the flask, washed with distilled water, dried, and weighed. A loss in the weight of copper of 68.4 parts ($=2\text{Cu}$) is equal to 85.5 parts of chlorine in the bleaching powder. This method is based on the fact that, under the conditions described, the chlorine of the bleaching powder first changes the iron protochloride into perchloride, which in its turn is again reduced to protochloride by the metallic copper, whereby some of the latter becomes dissolved. Every 2 equivalents of copper dissolved in this way are equivalent to 1 equivalent of chlorine in the bleaching powder.

Estimation of Chlorate in Bleaching Chlorides.

M. E. Dreyfuss bases a process on the property of cupric oxide in a strongly hydrochloric solution of being reduced to cuprous oxide by the action of stannous chloride at a boil. The end of the operation is marked by the decolouration of the liquid, which from yellow becomes colourless. For the process are required:—

1. A solution of copper made by dissolving blue-stone in distilled water, so as to make up a litre, of which 10 c.c. represent about 0.1 gramme of metallic copper.

2. An acid solution of stannous chloride made by dissolving 15 grammes of this body in 200 c.c. of hydrochloric acid, and making up to a litre with distilled water.

3. A solution of potassium chlorate. 5.917 grammes of this salt are dissolved in a litre of distilled water. 10 c.c. of this liquid are exactly equal to 0.05 gramme calcium chlorate.

To find the value of the cupric solution in comparison with that of

potassium chlorate, 10 c.c. of the solution of copper (0.1 gramme of copper) are poured into a flask or a conical colourless glass holding 150 c.c., and 50 c.c. of hydrochloric acid are then added. The mixture is heated to an incipient boil, and titrated with the standard liquid till decolourised. To the colourless liquid are added 5 c.c. of the potassium chlorate, which oxidise a corresponding quantity of cuprous chloride. This quantity is estimated again by titrating with stannous chloride. By this titration is found the relation between the cupric and the chlorate solutions. When this relation is once found it does not vary as long as the solution lasts.

Preparation of the Sample of Chloride of Lime.—Ten grammes are stirred up in 100 c.c. of water and saturated with ammonia, which is added by small quantities till there is a slight excess. It is then boiled till the odour disappears, and the liquid, with the precipitate, is poured into a flask marked at 500 c.c. The liquid is allowed to settle, depositing a precipitate which contains a little ferric oxide.

The introduction of a little potash into the chloride after it has been saturated with ammonia much facilitates the settlement of the deposit. When the solution of the chloride is thus prepared we proceed to titrate; 10 c.c. of the cupric solution are raised to a boil with 50 c.c. of hydrochloric acid, and titrated to decolouration with the stannous chloride. Then 50 c.c. of the solution of settled chloride are added; the mixture is boiled, and the copper which has been oxidised is titrated again. This method is applicable also to liquid chlorides.

Detection of Arsenic in Hydrochloric Acid.

Take a thoroughly clean and dry test-tube, of not too narrow a bore; put into it as much pure tin protochloride as can be placed on the point of a knife; next add from 4 to 6 c.c. of the hydrochloric acid to be tested; add, after this, gradually from 2 to 3 c.c. of pure concentrated sulphuric acid, taking care to move the test-tube very gently. If a white precipitate ensues, the addition of a few drops of the hydrochloric acid will be required to restore the liquid to perfect limpidity. If no arsenic is present, the liquid remains clear and colourless, even after standing for a time; but if even a trace of arsenic is present, the fluid becomes at first yellowish, next brownish coloured, and at last the metallic arsenic is deposited as a deep greyish-brown flocculent substance. Even with only $\frac{1}{100000}$ part of arsenious acid a colouration ensues. It is essential that when the sulphuric acid is added the liquid should become hot; if, therefore, that acid is too dilute to cause heating, the test-tube and contents should be warmed over a spirit-flame.

Purification of Hydrochloric Acid from Arsenic.

1. *Preparation of Weak Acid.*—In the preparation of weak acid it is only necessary to boil the commercial arseniferous acid in a flat-bottomed dish until the acid is reduced to two-thirds its original volume.

By allowing the hydrochloric gas to escape without collecting it, all the arsenic is taken with it in the form of terchloride, and the liquid remaining in the dish is no longer arseniferous; 8 litres of commercial acid, treated in this way, furnish in less than three hours 2 litres of acid free from arsenic.

2. *Preparation of Fuming Acid.*—Into a flat-bottomed vessel of 6 litres capacity, first pour 3 litres of the arseniferous acid, and add 0·8 gramme of powdered potassium chlorate (0·1 gramme per litre). Then adapt to the mouth of the flask a cork pierced with two holes, into one of which fit a straight and strong safety-tube; and into the other a larger tube, of the diameter used in organic analyses, 0·5 mètre long, and serving, so to speak, as a vertical elongation. This lengthened tube should be very little tapered at its lower part; fill it with about 100 grammes of red copper turnings well beaten down to within 0·07 metre of its upper orifice, and then fill almost up with asbestos or broken glass. Pass the greater part of this tube through the neck of the flask, so that as much as possible of the surface may be heated by the hydrochloric vapour. Then furnish the upper part of the elongated tube with a tube to carry the gas into a receiver. In traversing the column of copper the acid gas is deprived of its chlorine, and arrives in a pure state in the water destined to dissolve it. The mode of operation is very easily comprehended. By boiling the acid the transformation of the arsenic chloride into fixed arsenic acid is completed by the decomposition of potassium chlorate; the excess of chlorine is taken with the moist hydrochloric gas into the copper, which most readily absorbs it, in preference to the acid, for which its affinity is much less. The copper chloride returns to the flask in the form of a solution, while the gaseous hydrochloric acid condenses in the distilled water. But as it is important that there should always be in the boiling acid a slight excess of chlorine, to prevent the reduction of the arsenic acid, a constant current of hydrochloric acid, to each litre of which 1 gramme of potassium chlorate has been added, should arrive through the safety-tube (which should not dip more than from 8 to 5 c.c. into the liquid) so as always to maintain a small excess of chlorine, and at the same time to replenish the flask with hydrochloric acid to be purified. Generally the proportion of liquid acid thus added should be greater than is required for distillation, otherwise there might be an insufficiency of chlorine. When the experiment has been successfully performed the hydrochloric acid contains neither arsenic nor chlorine.

By this apparatus pure hydrochloric acid may be constantly obtained without any sensible loss of acid, and the process may thus be applied commercially.

8. Into the crude acid to be purified pass a current of sulphuretted hydrogen until all the arsenic is precipitated. Separate the arsenic sulphide either by subsidence and decantation, or by filtering it through

a funnel packed with asbestos. Remove the excess of sulphuretted hydrogen from the filtered liquid by the addition of a concentrated solution of iron sesquichloride, which destroys the sulphuretted hydrogen, being reduced to protochloride. Finally, rectify the acid from fixed-matters.

See also the chapter on Arsenic, p. 420.

Detection of Free Hydrochloric Acid in Solutions of Ferric Chloride.

Professor Nicola Rease finds that a solution of ordinary phenol treated with ferric chloride takes an amethyst colouration, turning to a brown. But if a drop of hydrochloric acid is added to the solution, the liquid either assumes no colouration at all or takes a greenish tint. He proceeds as follows:—1 gramme of the crystalline phenol of commerce is heated in 100 c.c. of pure water. He then pours 1 c.c. of the liquid ferric chloride into 50 c.c. of pure water. This solution being in a small test-beaker set on a sheet of white paper, the solution of phenol is added drop by drop. The first drop, if the solution is slightly acid, produces a fugitive colouration, but if it is strongly acid no colour appears. On continuing to add the phenol solution the colour becomes permanent and gradually darkens. From the volume of the phenol solution consumed an approximate idea of the quantity of acid present may be formed.

On the Detection of Hydrochloric Acid by Sulphuric Acid and Acid Potassium Chromate.

Mr. H. W. Wiley finds that this well-known test is more conveniently applied in the following way than by distillation in a retort as usually directed. Two small beakers are taken, of different sizes, the smaller of which will fit into the larger, leaving a space of two or three centimetres between the two bottoms. The chloride and chromate are well rubbed together, and placed in the larger beaker, care being taken that none of the particles touch the sides of the vessel. A few drops of oil of vitriol are added, and the smaller beaker then put in place. A lump of ice and if necessary a little salt, are then placed in the inner beaker. The chlorochromic acid is given off at a very gentle heat much below the boiling point, and is readily condensed on the cold surface of the beaker. If there is more than a mere trace of chloride, a watch-glass can be substituted for the smaller beaker.

After the reaction has ceased the inner beaker is removed. With a stirring-rod a very little oil of vitriol is placed on a white porcelain surface, and near by a minute crystal of strychnine. The end of the stirring rod is then moistened with the chlorochromic acid and brought into contact with the sulphuric acid and strychnine. The colour test for strychnine is developed with even greater brilliancy than with potassium chromate: the merest trace of a chloride is most un-

mistakably revealed by this test. If bromides are present, they do not at all interfere with the above reaction. Bromine itself with strychnine and sulphuric acid gives no play of colours. Bromides, moreover, when present, can usually be detected at the same time with the chlorides. The bromine formed is readily condensed, and forms either distinct globules or imparts a deeper colour to the chlorochromic acid. With iodides the case is quite different. In many cases no trace of chlorochromic acid has been found, when both chlorides and iodides were present. At other times, the iodine which is set free seems to be dissolved in the chlorochromic acid. In such cases, on adding ammonia to the reddish-yellow distillate, the whole turns black, from the formation of nitrogen iodide.

Valuation of Potassium Chlorate.

After having proved the absence of heavy metals, those of the alkaline earths, and sodium, a certain quantity of the chlorate to be valued is dissolved in water. Some dilute sulphuric acid is then added to the solution, and a piece of zinc is placed in the mixture. The nascent hydrogen immediately transforms the dilute chloric acid into hydrochloric acid. In about half an hour the undissolved zinc is withdrawn from the liquor, the sulphuric acid is precipitated by barium nitrate, and the zinc and excess of barium by means of sodium carbonate. The hydrochloric acid in the filtered solution is then estimated volumetrically by a standard solution of silver nitrate. A convenient solution is made by dissolving 1.887 gramme of silver nitrate in a litre of water, each c.c. of which solution will correspond to 1 milligramme of potassium chlorate.

If the chlorate contains chloride, this chlorine is first precipitated by silver nitrate, any excess of silver being removed from the filtered solution by sulphuretted hydrogen. The liquor filtered from the silver sulphide may then be treated with zinc and sulphuric acid, as described above.

FLUORINE.

Detection of Fluorine in Water.

Treat the solid residue of a large quantity of the water with an excess of concentrated sulphuric acid, and pass the gaseous products into slightly ammoniacal water. If fluorine is present in the water, some gelatinous silica is precipitated in the liquid, resulting from the decomposition of the silicon fluoride which was disengaged from the residue.

Estimation of Fluorine.

1. For estimating fluorine in combinations easily attacked by sulphuric acid proceed as follows:—Cover the platinum capsule in which the decomposition takes place with a funnel, resting with the capsule

on a platinum basin, on which it is fastened with wet plaster ; ascertain the weight of the funnel and the composition of the glass of which it is made. Heat the whole until most of the sulphuric acid has been expelled ; then raise the funnel, wash it carefully, dry and weigh it ; the decrease in its weight is owing to a portion of the glass having been attacked ; and as its composition was first ascertained, the weight of silica which has been attacked may be calculated from the decrease in weight, and, consequently, the quantity of hydrofluoric acid which has been disengaged. This method has given very satisfactory results with triplite of Limoges, and with zivieselite, and other analogous phosphates of Schlaggenwald. With calcium fluoride and cryolite too little fluorine is found, because the decomposition of these minerals is complete only when the mixture is properly shaken, which is difficult with the apparatus described above. The same funnel may be used many times, and is even better after it has been corroded.

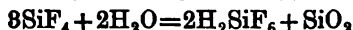
If the substance to be analysed contains silica, the quantity must be ascertained and added to that of the glass attacked, to obtain the weight of fluorine.

2. Place the substance to be analysed in a rather deep platinum crucible, and cover it with 3 or 4 times its weight of silica ; add a few drops of sulphuric acid, and heat gently for half an hour ; then gradually increase the heat until most of the sulphuric acid is expelled. Then treat the whole with hydrochloric acid, add some water, and leave it to deposit ; collect the deposit, calcine, and weigh it, and the loss of silica will indicate the amount of fluorine contained in the substance analysed (88 of fluorine correspond to 90 of silica).

For the estimation of fluorine, Professor A. Liversidge decomposes the fluoride by concentrated sulphuric acid in presence of silica, and passes the silicon fluoride formed into ammonia, the quantity of silica carried over being then estimated and the fluorine calculated therefrom. The powdered mineral is introduced into a platinum retort together with the needful quantity of sulphuric acid and finely-divided silica. It is heated first in the water-bath and then at $160^{\circ}\text{C}.$, the gaseous silicon fluoride formed being decomposed by passing it through a solution of ammonia. The last traces of the gas are carried over by drawing a current of air through the apparatus. The ammonia solution is gently evaporated in a platinum dish till the gelatinous silica passes entirely into solution, and it can then be precipitated as potassium silica fluoride by the addition of potassium chloride and alcohol.

Volumetric Estimation of Fluorine.

Mr. S. L. Penfield has made the well-known reaction



the basis of a volumetric estimation of fluorine, estimating the quantity of hydrofluosilicic acid formed from a given weight of fluoride by means of a standard alkali solution.

It is impossible to titrate the hydrofluosilicic acid directly, because as soon as an alkaline reaction is reached the silicofluoride is decomposed and an acid reaction is indicated, which change goes on slowly. But when barium chloride and an equal volume of alcohol are added to the solution, barium silicofluoride is precipitated from the solution, and an equivalent amount of hydrochloric acid is liberated, which can be titrated; by this means, using litmus as an indicator, very satisfactory results have been obtained, but the turbidity caused by the barium silicofluoride interferes with the change of colour of the litmus.

It has been found that potassium chloride possesses some advantages over barium chloride. On adding potassium chloride and an equal volume of alcohol, potassium silicofluoride is precipitated from the solution, and an equivalent of hydrochloric acid is liberated, but the potassium silicofluoride is a very transparent precipitate, and does not interfere with the change of colour of the indicators.

It is necessary that alcohol shall make up at least one-half the volume of the liquid to be titrated, so as to precipitate the potassium silicofluoride as completely as possible.

The apparatus needed is very simple, and consists of a gasometer of 10 or more litres capacity, a few flasks of about 150 c.c. capacity, a few large plain U-tubes 18 centimetres long and $2\frac{1}{2}$ centimetres diameter, made without any narrowing in the bend, and a heavy iron plate supported properly, so that it may be heated with a lamp.

The fluoride is weighed out accurately into one of the flasks; unless it is a silicate, 10 grammes of powdered and ignited quartz are added, and 2 or 3 pieces of quartz about the size of kidney-beans. These last facilitate mixing up the powder when the flask is shaken. The contents of the flask are then drenched with from 80 to 40 c.c. of sulphuric acid which has been previously heated and allowed to cool. The flask is tightly closed with a doubly-perforated cork; from the gasometer dry air is passed into the flask by means of a glass tube which reaches nearly to the bottom. The silicon fluoride mixed with air passes from the decomposing flask first through a small U-tube, made from ordinary glass tubing, 5 millimetres in diameter, and kept cool by being placed in a beaker of cold water, then into one of the large U-tubes intended for decomposing the silicon fluoride and absorbing the hydrofluosilicic acid. The U-tube contains a solution of potassium chloride mixed with an equal volume of alcohol; the escaping gas is made to bubble through this, and to ensure complete decomposition a second smaller U-tube is attached to the first: the first tube absorbs nearly all the acid, the second contains only traces. The decomposing flask is supported on the iron plate; by its side is placed a second flask containing sulphuric acid and a thermometer supported so that its bulb dips into the acid; the lamp heating the plate is placed midway between the flasks, and the heat is regulated so that the temperature of the acid remains between 150° and 160° C.

The decomposition is continued 2 hours in ordinary cases, and during that time a continuous current of air is forced through the apparatus, amounting to from 5 to 6 litres for the 2 hours, while the contents of the decomposing flask are frequently agitated by shaking.

After the decomposition and aspiration are completed, the contents of the U-tubes are titrated. For this purpose they may be transferred to a beaker, the tubes being rinsed with alcohol and water, or better, the acid may be titrated directly in the U-tubes. In order that the alcohol may make up one-half the volume of the liquid after the titration is completed, add a few c.c. of alcohol before titrating, or where 15 or more c.c. are to be added use a standard alkali one-half of whose volume is alcohol. As the separated silicic acid sticks to the sides of the U-tube, it is necessary to have prepared a glass rod bent a little at one end to scrape off and break up this silica.

A simple dry U-tube between the decomposing flask and absorbing tube is sufficient to condense any sulphuric acid that may go over from the heated acid.

When the fluorine is to be estimated in a mineral containing chlorine, as in the case of an apatite, substitute for the empty U-tube one filled with fragments of pumice impregnated with perfectly anhydrous copper sulphate. This will intercept any hydrochloric acid, and will also serve to condense any sulphuric acid vapour that may go over from the heated acid. The calculation is very simple. Each equivalent of sodium carbonate equals 1 equivalent of hydro-fluosilicic acid or 6 of fluorine.

The qualitative search for fluorine in substances free from silica is easily made, with small quantities of matter, in a platinum crucible furnished with a lid with a small circular hole pierced in the centre, above which a disc of glass is placed.

For the detection and estimation of fluorine in apatite, see p. 48.

CHAPTER XIII.

CARBON, BORON, SILICON.

CARBON.

Assay of Animal Charcoal.

THE points of greatest importance in an analysis of animal charcoal are the carbon, the carbonates, and the iron; the decolouriser, the neutraliser, and the destroyer. Under certain circumstances sulphates may be included, and in the case of unused charcoal the salts soluble in water should also be carefully estimated. The amount of phosphates is comparatively unimportant. The following is the process recommended by Dr. Wallace; it was frequently verified during the progress of the author's work on beet-root sugar and the chemistry of sugar-refining.¹

Carbon.—Five grammes of animal charcoal are dried at 220° F. in a hot-air bath or paraffin-bath; the loss of weight gives the moisture, which, subtracted from the loss by calcination, furnishes the proportion of carbon.

Calcium Carbonate.—This can be quickly and accurately estimated by well-known processes.

Iron.—After some little practice the iron can be safely estimated by Penny's process, using a very dilute solution of bichromate. The iron is always in a state of protoxide, faint traces of peroxide excepted, owing to the reducing action of the carbon in the re-burning.

Soluble Salts.—Fifty grammes of animal black are weighed and thrown into a little stoppered flask containing about 50 c.c. of distilled water; this is well shaken for a few minutes, and then filtered. The insoluble residue is re-digested in a fresh quantity of water; and this is repeated several times, so as to eliminate the whole of the soluble salts. The filtered liquid is evaporated over the sand-bath in a little porcelain capsule; the dry residue is weighed, and its weight gives the proportion of soluble salts. These salts consist of alkaline chlorides, sulphates, and carbonates; they also contain traces of calcium sulphate and sulphide.

¹ 'The Manufacture of Beet-Root Sugar in England and Ireland,' by William Crookes. London: Longmans and Co., 1870.

Estimation of the Decolourising Power of Animal Charcoal.

In these estimations the object is to carry out the operation in such a manner as to obtain, as nearly as possible, the same results on the small scale in the laboratory as in the manufacturing operations; and it is because many little precautionary measures which tend towards the attainment of that equality are usually omitted in the laboratory that such conflicting and apparently inexplicable results are recorded.

Mr. Arnot gives the following precautions to be observed so as to obtain trustworthy results:—

1. It must be decided what the results are to express: whether the relative decolourative power of equal bulks or equal weights of the charcoals, irrespective of size and proportion of grain, of the chars uniformly freed from dust, say by a 50-mesh sieve; or of equal weights of equal grains.

2. According as either of these alternatives is decided upon, the various samples must be thoroughly and intimately mixed, and, if necessary, brought to a uniform dryness and temperature. It is always safest to have them thoroughly dry, and at the temperature of the surrounding air.

3. The various samples are next to be put into glass tubes (tin may be used, but they preclude observations of a very important kind) provided with perforated false bottoms, covered with layers of cloth, and with taps capable of being accurately regulated. The tubes ought to be about 2 inches wide and 2 feet long, as nearly of the same diameter as possible. The best method of filling them is by passing the charcoal through a funnel, keeping the spout of the funnel moving constantly in a circular direction, so as to have the large and small grains equally diffused throughout. To allow the charcoal to run down either at one side, or, to a less degree, in the middle, is to cause to a certainty a separation of the larger grains from the smaller, and thus to create channels through which the liquor has too easy access.

4. See that no one tube is touched or shaken more than the others, after the charcoal has been put in.

5. Sufficient brown sugar liquor, of say 24° B., must be prepared, either by diluting raw filtered liquor from the sugar-house to that gravity, or by dissolving as much of an average quality of raw material as will make sufficient liquor for the whole experiment. In the case of preparing it on the small scale, albumen must be liberally used, and the liquor passed through paper filters—coarse French paper answers best. The albumen should not be added till all the sugar has been dissolved, and the temperature at, say, 160° F. An equal quantity of the prepared liquor, as nearly 180° F. as possible, must now be poured uniformly upon the charcoal in each tube.

The rapidity with which the liquor passes through the charcoal in each case may be noted. Care must be taken to have the top of the

charcoal always covered with liquor, and the taps below open. As soon as the liquor begins to drop at the taps they are closed.

6. The tubes being fully charged with liquor (there should be as much left on the top of the charcoal as will serve to force out the liquor in the charcoal), they are put into a cistern of water at 140° F., the water in which will rise to about 1 inch from the mouths of the tubes; the time is noted, and the cisterns, which ought to be felted, are covered.

7. At the end of not less than 1 hour (longer than 1 hour is sometimes advantageous, particularly if the raw liquor was very brown) the tubes are withdrawn, placed in their stands, and about 2 ounces of liquor run off each; this may be rejected, as the portion between the false bottom and taps is often turbid, and in addition has not been in contact with the charcoal for a sufficient length of time. The remainder of the liquor, i.e. so much as has actually been in contact with the charcoal, may now be run off in three successive quantities for comparison. The results may be compared with any set of standard colours, and recorded accordingly.

8. If these results are not sufficiently conclusive, a further quantity of raw liquor may be run on each tube, and the whole transferred as before to the water-bath, which, if felted, will still be hot enough. The second quantity of liquor will be run off with the same precautions as the first, and the results will show the relative *persistence* of the charcoal under trial.

If the taps are large the liquor will be likely to run off too rapidly, and, in that case, they had better be partially and uniformly closed. If it is found that the liquor runs through one sample particularly slowly, and through another particularly fast, it is quite admissible to assist the one by suction, and to check the other by closing the taps; but this should not be done unless in extreme cases, and the fact of having so assisted or retarded the process should always be noted.

It is scarcely necessary to mention the several points wherein the foregoing differs from the course usually pursued in testing charcoal, and yet it may be useful briefly to indicate some of these. Too little care is usually bestowed upon the selection and preparation of the samples. The tubes are, as a rule, too small: the charcoal cannot be run so uniformly into small tubes as large ones. The samples once charged with liquor are not usually kept warm: it is essential that they should be. Some charcoals act powerfully at low temperatures, while others require a considerable amount of heat to bring out their maximum decolourative power. Care must, however, be taken that the temperature employed does not exceed that attained on the large scale in the refining process. One sample of charcoal, known to be of very inferior decolourative power on the working scale, persistently gave results, by the usual method of testing in the laboratory, equal to the very finest charcoal obtainable, but when kept at an elevated tem-

perature, along with the finer samples, in the manner indicated above, its inferiority was at once manifest. The facts in this case were that the inferior charcoal readily yielded *all* its decolourative power at the low temperature, while the finer samples required the influence of heat to call their whole power into action.

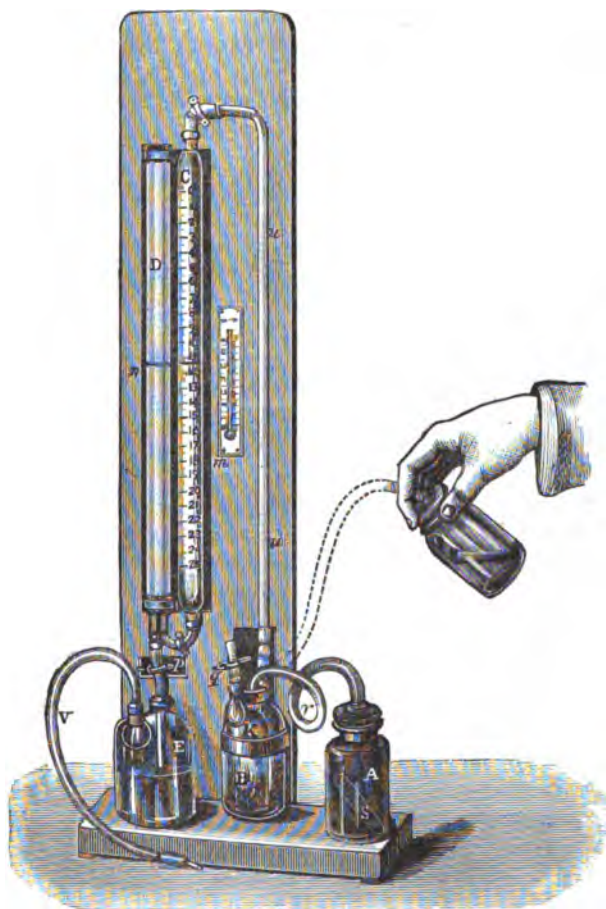
Volumetric Estimation of Carbonic Acid in Animal Charcoal.—Dr. Scheibler has devised a very perfect instrument which is adapted for the estimation of the quantity of carbonic acid contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily estimating the quantity of carbonic acid contained in animal charcoal. The principle upon which the apparatus is founded is simply this—that the quantity of carbonic acid contained in calcium carbonate can, according to well-known stoichiometrical rules, be used as a measure of the quantity of that salt itself; and instead of estimating, as has been usually the case, the quantity of carbonic acid by weight, this apparatus admits of its estimation by volume. It is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish. The analytical results obtained by means of this apparatus are very correct, provided care be taken to use the needful precautions.

The apparatus is shown in the annexed woodcut, and consists of the following parts:—The glass vessel *A*, serving for the decomposition of the material to be tested for carbonic acid, which, for that purpose, is treated with dilute hydrochloric acid; this acid is contained, previous to the beginning of the experiment, in the gutta-percha vessel *s*. The glass stopper of *A* is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube *r*, by means of which communication is opened with a three-necked tubulated bottle, *B*. The central neck of this bottle contains a glass tube firmly fixed, which is in communication, on the one hand, with *A*, by means of the flexible india-rubber tube already alluded to, and on the other hand, *inside* of *B*, with a very thin india-rubber bladder (similar, as regards thinness, to the very light and well-known inflated india-rubber balloons sold as toys). The neck, *g*, of the vessel *B* is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp; the only use of this neck of the bottle *B*, arranged as described, is to give access of atmospheric air to the interior of the bottle if required. The other opening is in communication with the measuring-apparatus, *C*, a very accurate cylindrical glass tube of 150 c.c. capacity, divided into 0.5 c.c.; the lower portion of this tube *C* is in communication with the tube *D*, serving the purpose of controlling the pressure of the gas; the lower part of this tube *D* ends in a glass tube of smaller diameter, to which is fastened the india-rubber tube *p*, leading to *E*, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring

clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can readily be done by blowing with the mouth into *v*, and opening the clamp at *p*.

The following apparatus and reagents are also necessary:—A small and very accurate weight for weighing off the substances to be tested ;

FIG. 12.



a thermometer ; hydrochloric acid ; a solution of ammonium carbonate ; and several small porcelain basins.

The main portion of the apparatus above described, with the exception, however, of the vessel A, is properly fixed by means of brass fittings to a wooden board, as represented in the woodcut. The filling of the apparatus with water is very readily effected by pouring it through a suitable funnel placed in the open end of tube D, care being

taken to remove, or at least to unfasten, the spring clamp at *p*; in this manner the water runs into *e*, which should be almost entirely filled. Distilled water should be used for this purpose, as the filling only requires to be done once, the water always remaining in *e* as long as the apparatus is intended to be kept ready for use. When it is required to fill the tubes *c* and *d* with water, so as to reach the zero of the scale of the instrument, remove the glass stopper from *a*; the spring clamp at *p* is next unfastened, the air is then blown by means of the mouth into the tube *v*, which communicates with *e*; by this operation the water rises up into the tubes *c* and *d*, which thus become filled with that liquid to the same height. Care should be taken not to force the water above the zero of the scale at *c*, and especial care should be taken against forcing so much of the fluid up that it would run over into the tube *u*, and thence find its way to *b*, as in this case a total disconnection of all the parts of the apparatus would become necessary. If by any accident the water should have been forced up above the zero at *c*, before the operator had closed the spring clamp at *p*, this is easily remedied by gently opening that clamp, whereby the water is allowed to run off to *e* in such quantity as may be required to adjust the level of the fluid in *c* precisely with the zero of the scale. The filling of the tube *c* with water has the effect of forcing the air previously contained in that tube into *b*, where it causes the compression of the very thin india-rubber ball placed within *b*. If it should happen that this india-rubber ball has not become sufficiently compressed and flattened, it is necessary to unfasten the spring clamp at *q*, and to cautiously blow air into *b*, through the tube *q*, by which operation the complete exhaustion of the india-rubber bladder placed within *b* is readily performed. This operation is also required only once, because during the subsequent experiments the india-rubber bladder *x* is emptied spontaneously. It may happen, however, that while the filling of the tubes *d* and *c* with water is being proceeded with, the india-rubber bladder *x* has become fully exhausted of air before the water in *c* reaches the zero of the scale; in that case the level of the water in the tubes *d* and *c* will not be the same, but will be higher in *d*. It is evident, however, that this slight defect can be at once remedied by momentarily unfastening the spring clamp at *q*.

The apparatus should be placed so as to be out of reach of direct sunlight, and should also be protected against artificial heat and sudden changes of temperature; the instrument is best placed near a north window, so as to afford sufficient light for reading off the height of the water in the tubes.

Hydrochloric Acid.—The acid required for the decomposition of the animal charcoal is poured into the vessel *s* for use during experiments. This acid need not be pure; the crude acid of commerce answers the purpose, provided it be diluted to a specific gravity of 1.12 at 17° C. For practical purposes it is sufficient to mix 2 parts

by bulk of water with 1 part by bulk of commercial hydrochloric acid.

Ammonium Carbonate.—In order to prepare the solution of this salt of the necessary strength, 1 part by weight of the ordinary ammonium carbonate of commerce is dissolved in 4 parts of water, and to this 1 part of liquid ammonia is added. The salt is first coarsely pulverised and immediately after placed in a bottle provided with a well-fitting glass stopper; the mixture of water and ammonia is next poured over the salt and the solution of the salt promoted by frequent shaking of the bottle. This solution of ammonium carbonate is used for the purpose of converting into calcium carbonate any caustic lime which might be present in the materials to be submitted to analysis.

Mode of Operating.—It is of the greatest importance that a good average sample, really representing the entire bulk of animal charcoal, be taken for investigation. This can be readily obtained by taking small samples, say a few ounces, from the filter (in sugar works) or from a cask, at various depths of the vessels containing the material; or, better still, if there be room, the charcoal should be placed in a heap on a large sheet of stout canvas, and well mixed together, and samples taken from various parts of the heap. These, if wet (as will be the case with charcoal just removed from the filters), should be dried by suitable means, and afterwards the whole sample should be coarsely ground and thoroughly mixed, and a portion taken for the purpose of being ground up to a very finely-divided powder, to serve the purpose of weighing a sample from. It is essential that the charcoal should be ground to a very fine powder, because this greatly promotes the decomposition by the acid.

There is supplied with the apparatus a metallic weight to serve as normal weight. This weight is placed in one of the pans of the balance (any balance, provided it be sensitive to from $\frac{1}{8}$ to $\frac{1}{16}$ of a grain, will answer the purpose); in the same pan a small porcelain basin is placed, and equilibrium is restored by means of small lead shot. As soon as the equilibrium is restored the normal or standard weight is removed from the pan of the balance, and there is placed in the small porcelain capsule remaining in the pan as much of the sample of bone-black to be tested as is required to restore the equilibrium. When several experiments have to be made consecutively, it is better to arrange beforehand the joint tare weight of the normal weight and of a watch-glass of suitable size, and to weigh off upon the latter the several samples. Dr. Scheibler recommends the transference of these weighed quantities to a porcelain capsule, because, according to his plan, the samples, after having been weighed, have to be thoroughly moistened with the solution of ammonium carbonate already referred to, in order to convert any caustic lime which might happen to be present in the material into calcium carbonate; but it is a decided improvement to moisten gently with the solution of ammonium carbonate a sufficient quantity

of the sample to be tested previous to weighing, to dry it, and to employ at last, for a few moments, a stronger heat short of redness (an air or fusible metal bath, heated to 240° C.), so as to obviate the chance of either an excess of ammonium carbonate or of water being present, while, at the same time, the decomposition of the calcium carbonate is guarded against. After the samples are quite cold, they are to be transferred to the flask or bottle A. Recent researches have shown that animal charcoal which has been once used for filtering purposes in sugar works no longer contains caustic lime, and the treatment with ammonium carbonate can therefore be dispensed with in that case, and need only be employed with samples freshly made.

The experiment for the estimation of the carbonic acid is carried out in the following manner:—First, the water in the tube c is made to stand exactly at the zero (0) of the scale; next, the weighed sample of the bone-black to be tested is transferred, with great care and without loss, to the bottom of the bottle A, which should be perfectly dry inside and quite clean. This having been done, the gutta-percha vessel s, which should also be previously well cleaned, is filled with the hydrochloric acid above referred to, to within from $\frac{1}{2}$ to $\frac{3}{4}$ inch from the top, care being taken not to drop any hydrochloric acid on the outside of the vessel; the gutta-percha vessel is next placed within the bottle A in a slanting direction, as shown in the woodcut; after this the glass stopper is replaced at A, care being taken to slightly grease it and the inside of the neck of A, so as to secure a better airtight fitting. The closing of A will (if all parts of the apparatus are properly tight) have the effect of slightly lowering the level of the water in c below the zero of the scale, while the water will rise just as much higher in d; by loosening, for a moment, the spring clamp at q, the normal height is properly restored. The operator should very carefully guard against handling or touching A after it has been once closed, because, by so doing, the warmth of his hand will cause the expansion of the air in A, and thereby affect the proper action of the apparatus. In order to cause the hydrochloric acid contained in the gutta-percha vessel placed inside A to run on to the animal charcoal, placed on the bottom of A, as described, the flask or bottle A is held by the neck, as shown in the woodcut. As soon as the acid comes into contact with the animal charcoal, the evolution of carbonic acid begins, and simultaneously the expansion of the very thin india-rubber bladder k, while the water in the tube c sinks, and correspondingly rises in d. While the bottle A is held in the right hand, as already indicated, and gently moved about so as to promote as much as possible the contact between the acid and the charcoal, the left hand is employed to gently open the spring clamp p, in such a manner as to run off towards e just as much water as is required to keep the level in the tubes c and d at the same height. Both these manipulations should be continued as long as any sinking of the level of the water in c is perceptible: in other words, as long as

any carbonic acid is given off. After this has quite ceased, and no change is perceptible, or any motion of the water in the tubes just alluded to has taken place, the operation may be considered at an end, care being taken, however, to keep the levels in the tubes c and d at precisely the same height. This having been done, the next step is to read off the height of the water at the scale on c, and simultaneously the thermometer.

Correction of the Volume Read off.—The Table on the following page contains in the first column the figures 1 to 25, which correspond with the numbers on the scale fixed to c; the next 19 vertical columns contain the figures indicating the percentage of calcium carbonate sought at temperatures from 12° to 80° C. If, for instance, the experiment has been made at a temperature of 16°, and the reading of the scale at c corresponded to 9°, this indicates a quantity of calcium carbonate of 9.08 per cent. Since, however, every degree at c is divided into 10 parts, it is quite possible to read off tenths of a degree, and the corresponding quantity of calcium carbonate is also found by the aid of the table referred to, under the first 9 figures of the column, by simply altering from the right to the left hand the decimal point; for instance, we have found at 14° C. 7.8° at the scale c; we therefore have for 7 units 7.09 per cent., and for $\frac{8}{10}$ 0.81 (because $8=8.11$), making together, for 7.8, 7.9 per cent. calcium carbonate.

Illustrative Examples.—

9.4° read off at c, at a temperature of 19° = 9.289 per cent. of calcium carbonate.

14.9° read off at c, at a temperature of 18° = 15.056 per cent. of calcium carbonate.

12.8° read off at c, at a temperature of 24° = 11.799 per cent. of calcium carbonate.

11.7° read off at c, at a temperature of 16° = 11.702 per cent. of calcium carbonate.

It is, however, for all practical purposes, quite sufficient to make round numbers of the figures following the decimal point, and instead of 9.289 to read 9.3; for 15.056 to read 15.06; for 11.799 to read 11.8; and for 11.702 to read simply 11.7.

The calcimeter is invaluable in cases where the frequent estimation of carbonic acid is required. With a little practice, 12 or 14 estimations may easily be made in an hour; and these, if upon the same finely-powdered sample, will, with ordinary care, be found to agree almost absolutely. The saving of time by this process over the most expeditious of the ordinary gravimetric methods will be found to be very great. Starting, in each case, with the sample in powder, the difference in time is such as easily to repay the first cost of the instrument by a few hours' work. As the instrument is supplied with a normal weight and tables of calculated results, no time is lost in after-calculations. The volume of carbonic acid and the temperature indi-

TABLE

For the Percentage Estimation of the Calcium Carbonate contained in Animal Charcoal, calculated from the volume of Carbonic Acid.

Observed Volume of Carbonic Acid	DEGREES OF TEMPERATURE (CENTIGRADE)																			
	13°	13°	14°	14°	15°	16°	17°	18°	18°	20°	21°	22°	23°	24°	25°	26°	27°	28°	29°	30°
1	0.80	0.80	0.79	0.79	0.79	0.79	0.78	0.78	0.78	0.77	0.77	0.77	0.76	0.76	0.75	0.75	0.74	0.74	0.73	0.73
2	1.88	1.87	1.86	1.86	1.86	1.85	1.84	1.83	1.82	1.81	1.80	1.79	1.79	1.78	1.77	1.76	1.75	1.74	1.73	1.72
3	2.95	2.94	2.92	2.91	2.90	2.89	2.89	2.87	2.86	2.85	2.83	2.82	2.80	2.79	2.77	2.76	2.74	2.73	2.72	2.71
4	4.01	4.00	3.98	3.96	3.94	3.93	3.91	3.89	3.87	3.85	3.83	3.81	3.79	3.77	3.75	3.73	3.71	3.70	3.68	3.66
5	5.07	5.05	5.03	5.00	4.98	4.96	4.93	4.91	4.89	4.86	4.84	4.81	4.79	4.77	4.75	4.71	4.69	4.67	4.65	4.63
6	6.11	6.09	6.06	6.03	6.01	5.98	5.95	5.92	5.89	5.86	5.83	5.81	5.78	5.75	5.72	5.68	5.65	5.61	5.58	5.56
7	7.14	7.12	7.09	7.06	7.02	6.99	6.96	6.92	6.89	6.86	6.82	6.79	6.75	6.72	6.68	6.65	6.61	6.58	6.53	6.51
8	8.17	8.14	8.11	8.07	8.03	8.00	7.96	7.92	7.88	7.84	7.80	7.76	7.72	7.68	7.64	7.60	7.56	7.53	7.49	7.47
9	9.19	9.16	9.12	9.07	9.03	8.99	8.95	8.90	8.86	8.82	8.77	8.73	8.68	8.64	8.59	8.55	8.50	8.46	8.42	8.39
10	10.20	10.16	10.12	10.07	10.02	9.98	9.93	9.88	9.83	9.79	9.73	9.68	9.63	9.57	9.52	9.46	9.41	9.35	9.30	9.25
11	11.20	11.15	11.10	11.05	11.00	10.95	10.89	10.84	10.79	10.74	10.68	10.63	10.57	10.52	10.46	10.40	10.35	10.30	10.25	10.20
12	12.20	12.15	12.09	12.03	11.98	11.92	11.87	11.81	11.75	11.69	11.64	11.58	11.52	11.46	11.40	11.33	11.27	11.22	11.16	11.11
13	13.20	13.14	13.08	13.02	12.96	12.90	12.84	12.78	12.72	12.65	12.59	12.53	12.46	12.40	12.33	12.26	12.20	12.14	12.07	12.01
14	14.20	14.14	14.07	14.01	13.94	13.88	13.81	13.75	13.68	13.61	13.54	13.48	13.41	13.34	13.26	13.19	13.12	13.05	12.99	12.92
15	15.20	15.13	15.06	14.99	14.92	14.85	14.78	14.71	14.64	14.57	14.50	14.42	14.35	14.27	14.20	14.12	14.04	13.97	13.90	13.83
16	16.20	16.13	16.05	15.98	15.91	15.83	15.76	15.68	15.61	15.53	15.45	15.37	15.29	15.21	15.13	15.05	14.97	14.89	14.81	14.74
17	17.20	17.12	17.04	16.97	16.89	16.81	16.73	16.66	16.57	16.49	16.41	16.32	16.24	16.15	16.07	15.98	15.89	15.81	15.72	15.64
18	18.20	18.12	18.03	17.95	17.87	17.79	17.70	17.62	17.53	17.45	17.36	17.27	17.18	17.09	17.00	16.91	16.82	16.73	16.63	16.54
19	19.20	19.11	19.03	18.94	18.85	18.76	18.67	18.59	18.50	18.40	18.31	18.22	18.13	18.03	17.94	17.84	17.74	17.64	17.55	17.46
20	20.20	20.11	20.02	19.93	19.83	19.74	19.65	19.55	19.46	19.36	19.27	19.17	19.07	18.97	18.87	18.77	18.66	18.56	18.46	18.36
21	21.20	21.10	21.01	20.91	20.81	20.72	20.62	20.52	20.43	20.32	20.22	20.12	20.01	19.91	19.80	19.70	19.59	19.48	19.37	19.27
22	22.20	22.10	22.00	21.90	21.80	21.70	21.59	21.49	21.39	21.28	21.17	21.07	20.96	20.85	20.74	20.63	20.51	20.40	20.28	20.18
23	23.20	23.09	22.99	22.88	22.78	22.67	22.56	22.46	22.35	22.24	22.13	22.02	21.90	21.79	21.67	21.55	21.44	21.31	21.20	21.10
24	24.20	24.09	23.98	23.87	23.76	23.65	23.54	23.43	23.31	23.20	23.08	22.97	22.85	22.73	22.61	22.48	22.36	22.23	22.11	22.00
25	25.20	25.08	24.97	24.86	24.74	24.63	24.51	24.40	24.28	24.16	24.04	23.91	23.79	23.67	23.54	23.41	23.28	23.15	23.02	22.90

cated by the instrument are referred to the tables, where the percentage quantity of carbonic acid or calcium carbonate is at once found. One great advantage of such an expeditious method as this is that there is no temptation to be satisfied with first results, as a few minutes suffice to repeat the process.

Volumetric Estimation of Carbonic Acid by a Modification of Scheibler's Apparatus.

Mr. E. Nicholson recommends the apparatus figured on the following page. For the second graduated tube of Scheibler's apparatus, with its outlet pipe, reservoir-bottle, and blowing-tube, Mr. E. Nicholson substitutes a reservoir which can be lowered as the pressure of gas forces down the column of water in the graduated tube. He dispenses with the diaphragm formed by the india-rubber bladder, relying on the impossibility of diffusion taking place beyond the double bulb during the short time which the operation requires. If the graduated tube be of 180 c.c., a quantity of gas equivalent to 0.5 gramme of calcium carbonate will not be beyond its capacity, at least in most European laboratories. The reservoir should be able to contain within its perfectly cylindrical part somewhat more than the quantity of water for which the tube is graduated.

To set the apparatus in working order, raise the reservoir (by means of the cord and counterpoise) until its lower end is $1\frac{1}{2}$ inch, or 1 inch below the zero of the graduated tube, and then pour in distilled water until the column rises to that point. Note the lower level of the water in the reservoir, consequent on the smaller calibre of the graduated tube: this difference for capillarity should be maintained at all readings of the column of water. When the column is under pressure, as at the end of an operation, the difference can, if necessary, be accurately adjusted by means of a scale corresponding to that of the graduated tube, and marked on the frame, or by a sliding pointer; but this is really unnecessary, for the allowance can be made with sufficient accuracy by the eye. Considering that the height of the column is only affected by less than one-tenth of the amount of error in the adjustment of the reservoir-level, the possible error in an adjustment by the eye is trivial. An error of a whole centimetre of height in the adjustment would affect the reading to the extent of 0.06 c.c. only. Even with a reservoir of varying calibre, the greatest possible error arising from defective adjustment for capillarity is well within 0.1 c.c.

Mode of Operating.—Into the flask or bottle used for the reaction, a weighed quantity of powdered carbonate is introduced, together with a glass or gutta-percha tube containing either 5 c.c. or 10 c.c. of diluted hydrochloric acid. The flask being connected with the apparatus, adjust the level of the water to zero, and then close the air-cock at the top of the bulb-tube. Holding the flask by the neck with the

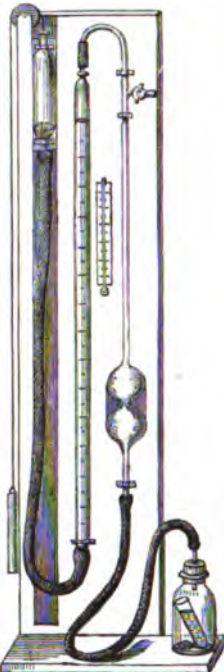
right hand, allow the acid to flow on to the carbonate while the left hand, on the cord of the counterpoise, lowers the reservoir as the gas forces the water down in the graduated tube. Agitate the flask as the action slackens, and when the column remains fixed, read off the height, the level of the reservoir being adjusted for capillarity. The operation being finished, disconnect the flask; raise the reservoir in order to drive carbonic dioxide out of the apparatus, and then open the air-cock; it may be left open until the next operation.

In the apparatus shown in Fig. 13 there is no air-cock, and the level of the water column, being depressed by the act of closing the flask,

FIG. 13.



FIG. 14.



cannot be brought to zero; the reservoir must therefore be lowered to the proper level, the height of the column read off, and the number deducted from that found after the operation.

The sources of possible error in estimations by this apparatus are:

1. From expansion of the gas disengaged in consequence of the heat produced during reaction.

2. From the absorption, or rather retention, of gas by the acid used for decomposition of the carbonate.

The first appears to be quite unimportant, except when the sub-

stance operated on contains much free base, as in the case of a partially-carbonated lime; when operating on such a substance, the flask should be immersed in *air-warm* water during the reaction. The second error can be ascertained and allowed for; Dr. Scheibler sets it down at 0.8 c.c. for 10 c.c. of acid, sp. gr. 1.12. It is better for each operator to ascertain the error for the acid he uses: let him make two sets of experiments with the same quantities of calcium carbonate, decomposing this in one set by 5 c.c., in the other by 10 c.c. of acid. 1 c.c. for 5 c.c. of dilute acid (diluted with its bulk of water) is a good allowance; it is, if anything, slightly under the mark. The volume

of gas obtained being corrected for absorption, the result may be calculated in two ways, as when the original apparatus is used. Either the experiment may be succeeded by a standard experiment on the same quantity of pure calcium carbonate (in this case there is no correction excepting for absorption, and a simple proportion gives the percentage), or the regular calculation may be applied.

Mr. R. Warington considers that Scheibler's apparatus is one of great practical value, as very speedy results, of fair accuracy, can be obtained by its use. The mode of calculating the results described by Scheibler must, however, be abandoned so far as the use of a fixed correction for the retention of gas in the fluid and the employment of Table I. are concerned. By substituting a correction proportional to the volume of gas obtained, and reducing the volume of gas into terms of the carbonate sought by means of Scheibler's Tables III.—VI., the errors thitherto made will be avoided. It is not at all pretended that the proportional corrections there given will be found to hold good at all temperatures: they are probably strictly true only for the temperature of the experiment. A far more complete series of observations is required. There are one or two points connected with the use of the apparatus which may be briefly mentioned. Any rise of temperature during the experiment entails a notable error, as the final reading is increased by the expansion of the whole volume of gas in the apparatus. A small rise in temperature is sure to take place if the operator stands before the instrument for 2 or 3 minutes while shaking the generating bottle. This may be avoided by placing a narrow glazed screen between the instrument and the operator. The generating bottle should also be wrapped in paper during the agitation. Bone charcoal, and many other substances in which carbonic acid has to be estimated, contain small quantities of sulphides; to prevent sulphuretted hydrogen being evolved a small quantity of mercuric chloride may be dissolved in the hydrochloric acid used.

Proximate Analysis of Coal.

An elementary analysis of coal teaches little with regard to the nature or practical value of the combustible. A proximate analysis, on the contrary, enables us to learn something in regard to the real nature of the coal. The moisture and ash are not only diluents of the fuel, but are in themselves obstacles to its effectiveness; the vapourisation of the moisture causes a serious loss of heat, whilst the ashes, by hindering complete combustion and by the heat they contain when dropped through the grate, constitute another loss. By further estimating the total amount of volatile matter we learn both the percentage of coke in the fuel and the amount of carbon (fixed combustible) and bitumen (volatile combustible matter). Although neither of these two products can be considered as simple chemical compounds, it is nevertheless of the utmost practical importance to

know these two quantities, because of the great value of coke and gas in manufactures. The proximate analysis of coals has been worked out very fully by Professor G. Hinrichs. Before he instituted his researches no investigation as to its accuracy, nor the best method of conducting the work, was known. In Europe reliance was placed almost exclusively on elementary analysis, whilst in the Government Surveys of the United States proximate analyses seem to have been almost as exclusively practised. But while the former may readily be turned into approximate estimations of the heating effects of the fuel, the latter have never been used for such purposes, nor until Professor Hinrichs's researches was it at all apparent that they ever could be thus made useful. It is evident that the useful applications of coal demand such an analysis, and it was therefore necessary for a rather extensive and thorough search into the method itself to be instituted in order to study its exact value.

It is easily seen that the following elements will modify the result of the amount of volatile matter driven off from a sample of coal contained in a covered platinum crucible:—Weight of coal and of crucible; degree and duration of heat; condition of coal. But notwithstanding all these elements this estimation admits of an accuracy of $\frac{1}{10}$ of a per cent., equal to that of weighing a gramme exact to the milligramme.

The sample of coal used in these preliminary experiments was not selected, but taken at random. From this sample a very pure piece, free from any visible admixture of either gypsum or pyrites, was selected. Its specific gravity was found to be 1.328.

Estimation of the Volatile Matter.—A common Bunsen burner is used for producing a red heat, and also a gas-burner with six jets, surmounted by a French *soufflet cylindrique*, for obtaining a white heat, care being taken to keep the gas-cock in the same position by means of an arm of 10 inches in length. These two sources of heat are denoted respectively 'BB' and 'Blast.'

The time is measured by means of a small sand-glass, running exactly three and a half minutes; this duration is denoted by *t*. Thus BB, *t*, means that the crucible was exposed to the constant flame of the Bunsen burner during three and a half minutes.

Influence of Quantity of Coal.—1. Coal, pulverised, not dried; heat BB, *t*; cooled and weighed; then blast, *t*; then weighed again.¹

N. of Exper.	Weight	Volatile matter, per ct.	Deviation	Crucible
<i>d</i>	5.860	48.24	−1.14	19.2
<i>n</i>	1.910	49.58	+0.20	19.2
<i>e</i>	1.147	49.87	+0.49	11.6
<i>o</i>	1.031	49.85	+0.47	9.4

Mean 49.88

¹ Weight = coal taken in grammes; crucible = weight of the same. Deviation per cent. from the mean given. These quantities are given in the same order in all subsequent tables, unless stated otherwise.

2. Coal in small fragments; heat as in 1.

N. of Exper.	Weight	Volatile matter, per ct.	Deviation	Crucible
<i>h</i>	3.743	48.30	-0.94	19.2
<i>g</i>	1.130	50.18	+0.94	9.4

Mean 49.24

For the same heat, the amount volatilised is greater as the mass heated is smaller; whether the coal is in small fragments or pulverised hardly makes any difference; but since the bitumen passes off more regularly when the coal is pulverised, while, when in fragments, slight explosions sometimes occur, the coal should be pulverised for the estimation of the bitumen.

8. Coal, pulverised, between 1 and 2 grammes; heat as above.

N. of Exper.	Weight	Volatile matter, per ct.	Deviation	Crucible
<i>n</i>	1.910	49.58	-0.19	19.2
<i>s</i>	1.147	49.87	+0.10	11.6
<i>o</i>	1.081	49.85	+0.08	9.4

Mean 49.77

giving as probable error of a single estimation only 0.108 per cent., or only 1 milligramme for 1 gramme of coal. This is not greater than that of the weighing itself, in which fractions of a milligramme were usually neglected.

4. Coal, pulverised (new portion), and between 1-2 grammes; heat, B B, *t*; immediately thereafter, blast, *t*, without cooling.

N. of Exper.	Weight	Volatile matter, per ct.	Deviation	Crucible
<i>a'</i>	1.16	50.86	+0.14	9.4
<i>n'</i>	1.04	50.58	-0.14	11.0

Mean 50.72

From 8 and 4 it is concluded that if the substance taken is from 1 to 2 grammes, the result will be constant for the same mode of heating.

Influence of Drying the Coal before Ignition.—5. Coal-fragments; heat, B B, *t*; not cooled; blast, *t*, with the probable error of one single estimation, 0.45.

N. of Exper.	Weight	Volatile matter, per ct.	Deviation
<i>t</i>	1.361	48.49	+0.76
<i>u</i>	1.060	47.26	-0.47
<i>v</i>	1.080	47.43	-0.30

Mean 47.73

Comparing this with 4 (same heating), it appears that about 8 per cent. less is volatilised by previous drying, and also that the accuracy of one estimation is four times less than when the coal is ignited without previous drying. In the arts, the coal is not artificially dried before coking. For all these reasons, the amount of volatile matter is best estimated on undried coal.

6. In general, it was found, as means—

4 dried	coal gave	47.97	per cent. volatile matter
10 undried	"	49.87	" " "

confirming the above.

Influence of Cooling after the Ignition over the Bunsen Burner, and before the Ignition over the Blast-Flame.—7. Coal, pulverised, not dried; heat, BB, *t*; then blast, *t*, without cooling.

N. of Exper.	Weight	Volatile matter, per ct.	Deviation
<i>x</i>	1.314	49.01	−0.03
<i>y</i>	1.156	49.05	+0.02

Mean 49.03

which, compared with the corresponding case, 8, giving the mean 49.77 and maximum deviation 0.19, shows that by the intermediate cooling about $\frac{1}{3}$ per cent. more is volatilised. This probably is due to the fact that the crucible upon cooling is filled with atmospheric air, which, upon renewed ignition, must burn a corresponding amount of coal.

Influence of Repeated Heating, the Crucible being after each Ignition Cooled and Weighed.—8. Coal = *r* = 1.628, in crucible 19.2, was dried, then ignited (BB, *t*), and lost 41.77 per cent. Being ignited again in the same way, it lost 2.76 per cent., or, in all, 44.53. Being successively ignited seven times, BB each time for six minutes, the total loss was 52.89, or, on the average for each of these six-minute BB ignitions, 1.12 (two of the estimations nearest this average were 1.06 per cent.).

Hereafter the same was exposed to the blast five times for three and a half minutes; the volatile matter passed off amounted to 57.81, giving for each of these last ignitions the average loss of 0.98 per cent.

It now had been ignited fourteen times, each time having been cooled and weighed; and we have fourteen ignitions, 57.81 volatile—first ignition, 41.77 volatile; hence, average for each of the thirteen ignitions, 1.195, or 1.2 per cent.

This series of experiments shows that it is impossible to heat coal until no further loss is sustained; for it is apparent that each heating, after complete cooling, produces, on the average, more than the additional volatilisation of 1. On 1 gramme of coal taken, 1 per cent. carbon burnt requires about 30 milligrammes, or 20 c.c. of oxygen. We may, therefore, consider these excesses almost equal losses due to a real combustion.

Influence of protracted Heating.—9. Coal, pulverised, not dried; heat, always first BB, *t*; and then immediately, without cooling, transferred to blast-lamp.

No. <i>a' + n'</i>	Weight (mean)	Blast 3 min.	Volatile matter	Difference	Difference per minute
<i>c'</i>	6	"	50.72	0.57	0.19
<i>b'</i>	9	"	51.29	1.04	0.35
<i>d'</i>	12	"	52.33	1.95	0.65
<i>e'</i>	30	"	54.28	2.93	0.16
<i>k'</i>			57.21		

By comparing each with the first mean, we obtain for each minute's blast after the first three, respectively—

0.24 0.39 0.27 0.2

showing less difference than the above.

The volatilisation, after the first three minutes' blast, is therefore increasing $\frac{1}{4}$ to $\frac{2}{3}$ per cent. for six minutes, and then very slowly decreasing to about $\frac{1}{3}$ per cent. for half-an-hour. At this rate the loss is 12 per hour.

It is apparent that the loss is less than when cooled in the intervals, but it proves that a slight current of air must get at the coal in the covered crucible.

At any rate it is demonstrated that the rule which is sometimes given, to heat until no further loss is sustained, demands an impossibility.

Influence of the Degree of Heat.—10. Coal, pulverised, not dried; heat, BB, t ; cooled and weighed; then blast, t ; cooled and weighed again.

After BB,

N. of Exper.	Weight	Volatile matter, per ct.	Deviation
<i>n</i>	1·910	48·08	+ 0·42
<i>e</i>	1·147	47·69	+ 0·08
<i>o</i>	1·081	47·23	+ 0·43
Mean . .		47·66	
Prob. error .		0·284	

After Blast.

N. of Exper.	Volatile matter per ct.	Deviation
<i>n</i>	49·58	— 0·18
<i>e</i>	49·87	+ 0·11
<i>o</i>	49·85	+ 0·09
Mean . .	49·76	
Prob. error	0·108	

showing that the higher temperature gives the most accurate results.

Result.—From these experiments it is concluded that—

The total volatile matter of coal is estimated with accuracy (1 milligramme on 1 gramme coal), by taking 1 to 2 grammes of undried, pulverised coal, heating it for three and a half minutes over a Bunsen burner (bright red heat), and then immediately, without cooling, for the same length of time over a blast gas-lamp (white-heat).

Estimation of the Moisture.—A flat-bottomed iron pan, of 20 centimetres in diameter, is filled evenly to the depth of $1\frac{1}{2}$ centimetres with sand, and the latter is covered with a copper plate, on which the watch-glass containing the coal is placed. A thermometer (scale to $370^{\circ}\text{C}.$) is, by means of an india-rubber stopper, inserted in an iron arm of the tripod supporting the iron pan, and held with its bulb about half a centimetre above the copper plate. By means of a Bunsen burner it is found very easy to keep the thermometer perfectly constant at $115^{\circ}\text{C}.$ This apparatus is a good substitute for Fresenius's iron plate.

The coal to be dried is finely pulverised, direct experiments having shown that the application of fragments is not only very much slower,

but also erroneous, on account of the peculiar property of bituminous coal treated of below.

These results show that the loss (called moisture) decreases regularly after the first hour of drying; that is to say, while the coal loses in weight during the first hour, it steadily gains in weight thereafter. It appears, furthermore, that the accuracy of an estimation, expressed in the smallness of the deviations from the mean, is greatest at the end of the first hour of drying, least after about three hours of drying, and thereafter increases again.

On account of these peculiar properties of bituminous coal, Professor Hinrichs advises that the loss in weight of the finely-pulverised coal after one hour's drying at a temperature between 105° and 110° C., should be put down as moisture.

For the analysis of coal and peat M. Sergius Kern gives a method well adapted for the laboratories of iron works, &c.

Estimation of Hygroscopic Water.—Three grammes of the substance in a finely-divided state are dried in a porcelain crucible placed in a beaker with a small quantity of sand on the bottom of it. The beaker is covered with a watch-glass, and the whole is placed on a sand-bath and heated for about 8 hours to a temperature of 110°. The end of the operation is easily known by the dryness of the watch-glass. The substance when dried is weighed, and the percentage of loss is next calculated.

Estimation of Carbon and Hydrogen.—The best process was found to be Liebig's: the ignition of 1 gramme of coal or peat with lead chromate in a tube of hard glass 0·25 metre long. The resulting carbonic acid, water, and sulphuric acid are passed through a potash apparatus containing caustic potash (1 part of potassic hydrate dissolved in 2 parts of water), and 2 U-tubes, the first containing ignited calcium chloride, the second a solution of lead nitrate. The increase in the weight of the potash apparatus and of the first U-tube will show the quantity of carbonic acid and water obtained. Knowing that carbonic acid contains 27·2 per cent. of carbon, and water 11·1 per cent. of hydrogen, the percentage of carbon and hydrogen may be easily calculated.

Calculation of the Calorific Power.—As 1 part of carbon in burning yields 8,080 calorific units, and 1 part of hydrogen in burning 84,460 calorific units, the calorific power of the coal may be quickly found.

Example.—Coal from Donetz mountains, near the village of Grouchevka, South of Russia :—

	Per cent.
Carbon	58·0
Hydrogen	11·0
Sulphur	1·0
Ash	23·0
Hygroscopic water	6·0
	<hr/> 99·0

For calculating the amount of calorific units in this coal proceed as follows:—

For carbon	$0.58 \times 8080 = 4686$
For hydrogen	$0.11 \times 34460 = 3790$

Total calorific units in the analysed specimen	8476
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On the Slow Oxidation of Coal.—An increase in weight after the first hour's drying is found in all Iowa coals. It was also found to occur in a sample of coal (Steinkohle) from Beuthen, Silesia, which showed a loss of 8.62 per cent. at the close of one hour, and in four further hours' drying gained again 0.42 per cent. It was not noticed in brown coal from Bilin, Bohemia, nor in anthracite from Pennsylvania. It is therefore probable that it is a property peculiar to pit coal.

Pyrites might well be the cause of this phenomenon: the red ashes obtained in many cases may be ascribed to pyrites disseminated through the coal in invisible particles.

From an examination of a large series of analyses, it has been found that the more ferruginous ash does correspond to a slightly greater increase in weight; but it is noticed also that this difference is very small as compared to the total amount of increase, being only $\frac{1}{2}$ to $\frac{1}{3}$ of the whole. Arranging these coals in the order of this hourly increase, it is found that the colours of the ashes do not at all form a regular series from white to red, as ought to be the case if this increase mainly depended upon the oxidation of the pyrites.

The greater increase of the pyritic coals is accounted for by the oxidation of the pyrites they contain; the comparatively great increase of coals giving a pure white ash seems to force the conclusion upon us that the bitumen of the coal itself oxidises, and that to this oxidation the main increase of all these bituminous coals must be ascribed. Bearing in mind the behaviour of bituminous coal from Silesia, anthracite from Pennsylvania, and brown coal from Bohemia, it seems not unlikely that this is another characteristic chemical difference between bituminous coals and other fossil coals.

Estimation of Ash.—Incineration and an accurate estimation of ash are, in many substances, attended with not inconsiderable difficulties. These may arise from the sparingly combustible nature of the bodies, as in the case of anthracite or graphite; from the presence of certain mineral substances which impede incineration, as silicic acid, phosphates, and fusible salts; from a tendency to decrepitation observed in many vegetable matters, and in all coals; from the partial volatility of various constituents of the ash, and from the chemical changes which the ash may undergo according to the degree and duration of the heat and the supply of air.

The first two of these difficulties affect principally the rapid execution of the process, whilst the remaining affect the composition of the

Ferric oxide	17.42
Lime	17.83
Magnesia	6.97
Sulphuric acid (saturating 4.018 lime)	5.94
Matter not estimated	2.00

1.049 gramme of this ash moistened with alcohol, and then ignited for a considerable time in the muffle at a white heat, decreased to 1.0465 gramme. On treatment with ammonium carbonate, and gentle reheating, the ash weighed 1.056 gramme. The ash effervesced a very little more with acids; a trace of calcium carbonate had been decomposed during incineration. The practical results of Dr. Muck's experiments may be stated as follows:

1. The chemical changes during the incineration of coal can only serve in rare and especial cases as an explanation of great differences in the estimation of ashes. For instance, when coal contains very much sulphur, and at the same time very little lime. In presence of much lime the combustion-products of the sulphur are more or less completely retained, whilst if little lime is present variable amounts of sulphur are driven off.

2. In case of a thoroughly homogeneous material, i.e. a finely-powdered and well-mixed average sample accurately and carefully analysed, the estimations of ash may be expected to agree to within 0.1 to 0.2 per cent.

Larger differences, except in the peculiar cases just referred to, must be referred to defective work or great difference of the samples.

It is understood that the proportion of moisture must be taken into consideration. In a thoroughly air-dry coal—not lignite—the highest limit of moisture is from 1 to 2 per cent.

The platinum crucible, according to the position of the flame, may be coated with soot. This coating may be easily burnt away, but care must be taken not to wipe a sooty place, nor a place that has been sooty, without carefully checking the weight of the crucible after weighing the ash. In the places where soot has been formed by the dissociation of the hydrocarbons the platinum becomes disaggregated and is coated with a black-grey deposit of finely pulverulent metal, which is easily rubbed off. The author has observed variations exceeding 8 milligrammes produced in this manner.

Determination of Specific Gravity.—Coarse fragments, freed by means of a sieve from all small particles, and averaging $\frac{1}{10}$ c.c. in volume, are introduced into a 50-gramme flask provided with a thermometer stopper. The constants for this flask for temperatures varying from 50° to 80° F. are previously carefully estimated.

The given specific gravity corresponds to the coal perfectly soaked, so that all its pores are filled with water. That requires, on the average, 12 hours, permitting two estimations per day,—one in the morning, another in the evening.

That this precaution is important may be seen from the following example :—2.76 grammes coal gave the specific gravity 1.309 at 64° F., immediately after filling the flask with water ; after about 12 hours' soaking, the specific gravity had increased to 1.328 for the same temperature. According to this latter estimation, a cubic foot of this coal would weigh 82.76 lb. ; according to the former, only 81.58, or 1.18 lb. less. This shows a considerable degree of porosity of the coal, and indicates the absurdity of giving the weight in pounds of a cubic foot of coal with four decimals, although no statement in regard to temperature or time of weighing is made.

Calculation of Results.—It may be sufficient here to state that, besides the percentage composition of the coal, it is proper to reduce the composition to the combustible = 100, in order to obtain a proper comparative estimate of the character of the fuel itself (in regard to the proportion of bitumen and carbon), and of the amount and quality of the impurities (ashes and moisture). It has also been shown that, for considerable areas of the coal-field, the sum of the constituents on the scale of combustible = 100 is the proper caloric equivalent, and that the percentage of the combustible in the fuel gives a proper estimate of its value.

Assay of Coal before the Blowpipe.

The blowpipe method is well adapted to the assaying of coal. Not only does the portableness of the apparatus make it very convenient for use away from home, wherever the balance can be set up ; but its use at home is quite as satisfactory on the score of exactness as the assay with the muffle or retort, or large platinum crucible and large balance. Mr. B. S. Lyman gives the following directions for carrying out this assay :—

Besides the ordinary pieces of the blowpipe apparatus, as made at Freiberg, all that needs to be made expressly for the coal assay is a small covered platinum crucible of the same size and shape as the clay crucibles of that apparatus ; and there must be a little ring for the crucible to stand on, of German silver, about $\frac{3}{8}$ of an inch across and half that in height. Such a crucible cover and ring weigh about $2\frac{1}{2}$ grammes more than the ordinary metallic cup that rests on the pan of the balance ; the crucible and ring without the cover weigh less than 2 grammes more than the cup. If it be desired to estimate the amount of hygroscopic moisture in the coal, a small drying-bath must be made too ; but the hygroscopic water in ordinarily well-dried coals (not brown coals) is of little importance.

The size of the crucible allows the coking of 200 to 600 or more milligrammes of coal, according to the dryness of the coal and the extent of its swelling up when heated ; and as the blowpipe balance weighs within $\frac{1}{10}$ of a milligramme, it is easy to weigh within much less than $\frac{1}{10}$ of one per cent. of the amount of coal assayed,—much

nearer, in fact, than the exactness of the coke assay in other respects. In this point, indeed, the blowpipe assay is quite as good as the assay with the larger balance, especially the muffle assay, where the coal must be brushed into a clay receptacle after weighing, and the coke or ash brushed off from it before weighing; whilst here the crucible is weighed each time without removal of its contents, and without danger, therefore, of losing anything or adding any dust. It may be objected that the smallness of the amount of coal that can be assayed with the blowpipe makes it a less trustworthy indicator of the general composition of the coal than a larger assay; but the size of the lumps or powder assayed may be made finer accordingly, so that when mixed up an equally just sample of the whole mass would be got for the small assay as for the large.

Anyone who has a little experience both in the use of the blowpipe and in the ordinary muffle assay of coal will scarcely need any further teaching for the coal assay with the blowpipe. For others, it is worth while to say that the coal may be assayed either in a fine powder or in little lumps, and either with a slowly-increasing or with a quickly-increasing heat. A quick heat will give less coke by several per cents., but will often make a dry coal cake together that would not cake with a slow heat. The cover of the crucible should be left open a very little way for the easy escape of the gas, but covered enough to prevent any flying off of solid material. The heat should increase to redness, and as soon as the escaping gas stops burning the heat should be stopped. As some coals part with their gas more quickly than others, of course no definite time can be fixed for heating all coals; but the burning of the gas is a sufficiently good sign. Care should be taken not to let the coke take up moisture from the air before weighing, as it will quickly do if it has a chance. Of course, owing to the different effect of quick or slow heat, a certain uniformity of result, even with perfectly uniform samples of coal, can only be got, without error, by practice and by mechanical skill, by reproducing with nicety the same conditions in successive assays.

After the coke has been weighed it can be heated again with very free access of air, say with the crucible tilted to one side, with the cover off, until everything is thoroughly burnt to ashes; and these should be re-heated until no change for the less is made in the weight. With free-burning, soft (semi-bituminous) coals this calcination is very slow, so that it is very fatiguing or even impossible to carry it out with the blowpipe; but in that case the crucible may be heated over a Bunsen gas-burner or an alcohol lamp, and left to glow for hour after hour. The coking is far more conveniently done in the same way than by blowing with the mouth.

As an illustration of the degree of accuracy which this method may be expected to give, the author adduces a pair of blowpipe assays, made five years ago, of some West Virginia asphaltum, that seemed

itself to be much more uniform in composition than coal from different benches in one bed is apt to be:—

	Volatile Matter	Coke	Ash
No. 1 .	47.29 per cent.	52.71 per cent.	1.65 per cent.
No. 2 .	46.93 ,,	53.07 ,,	1.81 ,,
Mean .	47.11 ,,	52.89 ,,	1.73 ,,

Estimation of Sulphur in Coal and Coke.

Mr. Crossley has drawn attention to the fact that the process of estimating sulphur in coke, &c., by boiling in nitric acid gives results much below the truth. In the same sample he found the process of fusion with nitre, sodium chloride, and potassium carbonate gave 0.608 per cent., whilst boiling with nitric acid yielded only 0.477; whilst in another sample fusion gave 1.23 per cent., and boiling with nitric acid 0.93 per cent. He has arrived at the conclusion that the cause of this loss is, not that some of the sulphur escapes oxidation, but that a portion is driven off by evaporation to dryness. Upon adding a little potassium nitrate to the nitric acid, for the purpose of fixing the sulphuric acid formed, and thus preventing its volatilisation on evaporation to dryness, the results appear to be as accurate as those yielded by the fusion process.

Dr. T. M. Drown uses bromine as an oxidising agent. He finds it especially valuable in the analysis of coal. By the treatment of coal as above described results are obtained which agree very closely. The coal, as such, is not attacked, and the sulphur obtained therefore, represents that existing in the coal as pyrites, and also as soluble sulphates. The residue left by this treatment has been subjected again to the same process, and yields no more sulphur. On combustion, however, or by complete oxidation, either by oxidising acids or by fusion, additional sulphur may be obtained, which must represent that combined organically with the coal.

In comparing the bromine method with others it was found that the treatment with hydrochloric acid and potassium chlorate gave on coals with but little sulphur in the form of pyrites the same results, but on coals with much pyrites the results were decidedly lower than by the bromine method. The action of nitric acid and potassium chlorate depends upon the nature of the coal. Some coals are converted partly into a brown unmanageable solution, and others are oxidised completely to a clear solution. In the latter case, of course the total sulphur could be obtained.

As was said above, the sulphur obtained by the bromine method represents both the sulphides and sulphates in the coal. The methods ordinarily given for the separate estimation of calcium sulphate are faulty. Sodium carbonate readily attacks pyrites, and dilute hydrochloric acid and even water, when heated for some time in con-

tact with pyrites, with access of air, contain notable quantities of sulphuric acid. It would seem, therefore, necessary to dissolve out the calcium sulphate by means of water, with the careful exclusion of air.

The estimation of the total sulphur in coal by means of fusion with alkaline carbonates and nitrates, or chlorates, is unsatisfactory, owing to the large amount of salts in the solution in which barium sulphate is precipitated. A much better method is to burn the coal in a platinum boat placed in a glass tube in a current of oxygen. The products of combustion may be absorbed by a solution of bromine in hydrochloric acid, or by a dilute solution of potassium permanganate. The latter gives equally good results with the bromine. It is absolutely necessary in this process, as originally pointed out by Muck, that the combustion-tube should be washed out with water after the completion of the combustion, since sulphuric anhydride condenses in considerable quantity in the tube beyond the boat. It is further necessary, of course, to fuse the residual ash with alkaline carbonates to estimate the sulphur which has not been volatilised by the combustion.

M. A. Eschka directs to powder as finely as possible 1 gramme of the sample, and mix intimately with 1 gramme of calcined magnesia and 0.5 gramme of anhydrous sodium carbonate. Heat over the lamp in an open platinum crucible, inclined so that only its lower half may be brought to a red heat. The ignition requires from forty-five to sixty minutes, and the mixture should be stirred every five minutes with a platinum wire. The process is complete when the ash becomes yellowish or brownish. Let it become quite cold, and mix intimately with the ash, by means of a glass rod, $\frac{1}{2}$ to 1 gramme of ammonium nitrate, and heat to redness for five to ten minutes, the crucible being covered with its lid. The residue is then placed in a precipitating glass and covered with water. The residue adhering to the crucible is detached by heating with the liquid, and the washings are added to the solution in the glass. The sulphuric acid is then estimated in the usual manner.

Valuation of Coal for the Production of Illuminating Gas.

Take 100 grammes of the coal in small lumps, so that they may be readily introduced into a rather wide combustion-tube. This is drawn out at its open end (after the coal has been put in) so as to form a narrow tube, which is to be bent at right angles; this narrower open end is to be placed in a wider glass tube, fitted tight into a cork fastened into the neck of a somewhat wide-mouthed bottle serving as tar vessel (hydraulic main of the gasworks). The cork alluded to is perforated with another opening, wherein is fixed a glass tube, bent at right angles, for conveying the gas, first through a calcium chloride tube, next through Liebig's potash bulbs containing a solution of

caustic potash, having lead oxide dissolved in it. Next follows another tube, partly filled with dry caustic potash, and partly with calcium chloride; from this last tube a gas-delivery tube leads to a graduated glass jar standing over a pneumatic trough, and acting as gas-holder. Before the ignition of the tube containing the coal is proceeded with, all the portions of the apparatus are carefully weighed, and next joined by means of india-rubber tubing. After the combustion is finished, which should be carefully conducted so as to prevent the bursting or blowing out of the tube, the different pieces of the apparatus are disconnected and weighed again. The combustion-tube has to be weighed with the coal after it has been drawn out at its open end, and with the coke after the end of the combustion when it is again cold, and for that reason care is required in managing it. We thus get the quantity of tar, ammoniacal water, carbonic acid, and sulphuretted hydrogen (as lead sulphide), and the gas is measured by immersing the jar in water, causing it to be at the same level inside and out. Empty the Liebig's bulbs into a beaker, and separate the lead sulphide by filtration, wash carefully, dry at 100°C ., and weigh. From the lead sulphide the sulphuretted hydrogen present is calculated. This process, devised by the late Dr. T. Richardson of Newcastle-on-Tyne, was found by him to yield very reliable results, so as to be suitable for stating what quantity of gas a ton of coal thus analysed would yield.

Coal Gas.

Detection of Air in Coal Gas.—Ten parts by weight of anhydrous manganous sulphate are put into a two-necked Woulf's bottle, and 20 parts of warm water then added to dissolve it. To this mixture is immediately added a solution of 10 parts by weight of Rochelle salt, dissolved in 60 parts of water; the thorough mixing of the fluids is promoted by well shaking of the bottle, after this a quantity of a solution of caustic potash is added, sufficient to render the fluid quite clear. Immediately after this perforated corks fitted with very tightly-fitting glass tubes are placed in the necks of the bottle, which should be entirely filled with the mixed fluid just alluded to. One of the glass tubes—the inlet tube for the gas to be tested—should just dip a little under the upper level of the fluid; the outlet tube, on the other hand, should only reach half-way to the perforation of the cork. A very slow current of gas is now made to pass through the fluid, and is kept going for at least a quarter of an hour, and at most one full hour.

In case the gas is quite free from atmospheric air, the fluid in the bottle will remain quite clear; if traces even of air are present, a faint colouration of the liquid will soon become apparent: with a larger proportion of air present in the gas, the fluid will soon be coloured, first light brown and afterwards intensely black. Since these

changes of colour are due to the oxidation of the manganese, it is evident that every care must be taken to avoid the presence or access of accidental air; the fluid in the Woulf's bottle should reach the cork. It is best to cool the bottle during the experiment with ice if at hand, otherwise with very cold water; the current of gas must be slow.

Estimation of Sulphuretted Hydrogen in Coal Gas.

An apparatus contrived by Dr. Wagner is used at the Munich Gas-works, to indicate the amount of sulphuretted hydrogen contained in crude gas. The following description is from the 'Journal of Gas-lighting':—¹

The apparatus consists of two glass flasks, E and A, a glass pipe, B, fixed upon a stand, and an aspirator. The first flask, E, contains a little acetic acid, for the absorption of the ammonia contained in the gas, and for the reception of the tar. The inlet pipe, *a*, is bent at an obtuse angle, to allow the condensed tar to flow into the flask, and after passing through an india-rubber stopper, the pipe descends to near the bottom of the flask, and dips into the acetic acid. The outlet-pipe, *b*, on the contrary, does not penetrate further than to within a short distance below the inner surface of the stopper, and is connected with the second flask, A, into which it enters, descending to nearly the bottom of it, by two bends and proper inclines. The second flask is about half-filled with a solution of lead acetate, made acid by acetic acid. The outlet-pipe, *c*, of this flask is at its upper end bent downwards, and is connected by an india-rubber tube with another smaller glass pipe, *d*, which passes through an india-rubber stopper, *e*, and penetrates into the pipe B to its lowest point, terminating in a fine end, so as to prevent the gas coming out otherwise than by a very narrow passage and in small bubbles. The pipe is about 1 metre long, and, as shown in the woodcut, is also filled with a solution of lead acetate. While the left extremity of this pipe is closed by the stopper, *e*, its right has a globe, *f*, at the end, for the deposit of any fluid that may have been carried over; and in continuation therewith is a glass tube through which the gas takes its course to the aspirator, *c*. This aspirator, which in this instance has a capacity of 12 litres, is closed by means of an india-rubber stopper, through which passes the inlet-pipe, *g*, bent at the top, the extreme end of which, going downwards, is connected with the glass tube near the globe *f* by an india-rubber tube. At the bottom of the aspirator a small lateral pipe is inserted, with an india-rubber tube, the latter being provided with a pressure-cock, together with a thumbscrew, for the purpose of discharging the water.

When the apparatus is used, the gas is admitted by a connecting

¹ See also the *Chemical News*, March 8, 1867, vol. xv., p. 112.

pipe between the hydraulic main and the condenser—nearest, however, to the former.

The cast-iron pipe is drilled at the upper part, and the $\frac{3}{4}$ -inch outlet lead pipe is carried upwards about 2 feet perpendicularly to convey

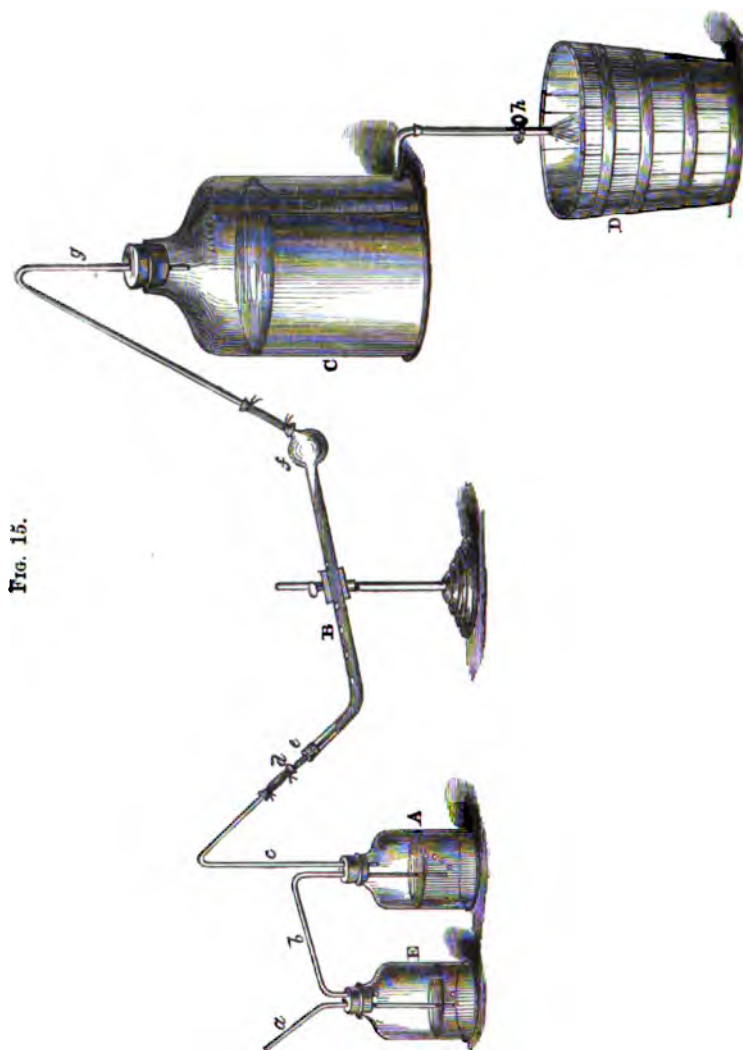


FIG. 15.

back into the cast-iron pipe a portion of the tar carried onward by the warm gas, but which soon becomes condensed. The lead pipe is then bent downwards, and carried about 10 feet in length to the experimental table, where it terminates with a stopcock. A short

india-rubber tube is drawn over this cock so as to allow of its being connected afterwards with the apparatus. Before an experiment takes place gas is allowed to flow freely for at least half an hour through the supply pipe, in order that the inner surfaces of the same may become completely covered with tar, thus insuring that the lead of the pipe does not decompose the sulphuretted hydrogen of the gas.

After filling both the flasks and the pipe in the manner before described with the absorbing fluids, and completely filling the aspirator with water, and making tight all the connections of the apparatus, the water is allowed, by opening the pressure-cock, *h*, to flow out of the aspirator until atmospheric air in the form of bubbles is sucked up by the apparatus, and until the level of the water corresponds exactly with one of the marked lines of the aspirator. The cock *h* is then again shut for a short time, and the loose end of the india-rubber tube fastened to the supply pipe is then drawn over the glass pipe *a*. It is of course premised that the pressure of the gas in the supply pipe is = 0, as is the case in establishments where exhausters are used. Upon the connection being restored between the apparatus and the supply pipe, the pressure-cock is again slightly opened and the gas allowed to pass gently—say about 20 litres per hour—until the water-level in the aspirator has descended to the line marked 1. The flow of the gas is kept up as uniformly as possible by the regulating screw of the pressure-cock. As at each experiment from 40 to 50 litres pass each time, it is necessary that the above experiment should be repeated several times. The pressure-cock and the cock of the supply pipe being again shut, the stopper of the aspirator is loosened, the aspirator again filled with water, and the entire operation repeated in the manner above described.

Where no exhausters exist, and where there is a pressure of several inches in the gas supply pipe, no aspirators are required, but a gas-meter is used instead.

In the first flask, *E*, filled with acetic acid, is collected the greatest portion of the tar; no absorption of sulphuretted hydrogen takes place here, as the crude gas enters it a high temperature. In the second flask, *A*, and also very slightly in the pipe *B*, a black precipitate is formed, composed partly of lead sulphide, partly of tar. The latter however, is apt to carry down with it a considerable quantity of the solution of lead employed. In order to bring the precipitate thus formed into a condition to be weighed, it is first filtered, then well washed, and dried at a temperature of about 100° C., and put into a small porcelain dish. Fuming nitric acid is then repeatedly poured over it, also at a temperature of about 100° C., and this is continued until the black mass has become quite white. When this has taken place, the residue of the nitric acid is driven off by evaporation at 100°. By the above operation the lead sulphide is converted into lead sulphate, the tar is destroyed, and the lead carried down by the tar is changed

into lead nitrate. Lead nitrate, on the contrary, is readily soluble. For this reason the white mass is washed with water in a porcelain dish, and the soluble nitrate separated by filtration from the insoluble lead sulphate. The latter, after being properly washed and dried, is heated in a crucible and weighed as lead sulphate, from which the sulphuretted hydrogen is readily calculated.

Detection of Carbon Disulphide in Coal Gas.—Dr. Herzog detects this body in the following manner:—A solution is prepared by saturating absolute alcohol with ammonia gas. Then a concentrated aqueous solution of lead acetate is made, and, to insure saturation, a small portion of the solid salt is left in contact. Both these fluids must be preserved in well-stoppered bottles.

The gas to be tested may be conveniently delivered from a length of vulcanised india-rubber tubing, to the end of which is adapted a narrow glass tube about 5 or 6 inches long. 5 drops of the lead acetate solution are then mixed in a test-tube, with about 60 or 70 drops of the alcoholic ammonia. No precipitate will be formed providing the latter solution has not been allowed to absorb any carbonic acid.

The glass tube delivering the supply of coal gas is now immersed in the mixed solution to a depth just sufficient to allow the gas to be forced out by the existing pressure, and to escape in small bubbles. In the event of carbon disulphide being present, the liquid becomes gradually coloured, and soon afterwards a yellowish-red precipitate is formed, which by longer action assumes a brownish colour. If carbonic acid exists in the gas, then a white precipitate is thrown down, which imparts to the yellow-red a somewhat lighter colour.

As a confirmatory experiment, the gas may be first passed through the alcoholic ammonia alone, and the lead solution subsequently added, when an orange-coloured precipitate, appearing either immediately or very shortly afterwards, will be formed if carbon disulphide is present. In order to meet the objection that sulphuretted hydrogen may perhaps have occasioned this reaction, let some of the gas be first passed through a small quantity of the simple lead solution. The smallest trace of sulphuretted hydrogen causes the blackening of the liquid, whereas carbon disulphide does not alter it in the slightest degree.

It should be mentioned that if the yellow-red precipitate be allowed to remain under the fluid, it gradually changes colour, and becomes white after the lapse of about 24 hours. If, however, the precipitate be filtered immediately slightly washed, and dried, it becomes a dark brown.

With regard to the explanation of the chemical reactions which occur in this process, the observations made by MM. Zeise and Debus may be considered to prove that, by the action of carbon disulphide on ammonia, according to the concentration and temperature of the fluids and the proportion borne by the ammonia to the sulphide, so will the

relative amounts of the products of decomposition vary. In concentrated solutions, and when ammonia is in excess, ammonium sulphocarbonate and ammonium sulphocyanide are formed; in dilute fluids and when carbon sulphide is in excess, ammonium xanthionate. Therefore, by this experiment one or other product will preponderate according to circumstances, dependent upon the larger or smaller quantity of carbon disulphide contained in the gas. In any case, lead compounds are formed corresponding to the ammonia compounds, which possess at first an orange-red and afterwards a golden-yellow colour.

Notwithstanding the complicated nature of the chemical reactions involved in the testing of gas by this process, its adoption is to be recommended on account of the practical simplicity which has attended the working of a great number of comparative experiments.

Detection of Sulphur in Coal Gas.—On forcing, by an ordinary blowpipe, the flame of coal gas for about a minute on to distilled water containing a little acid barium chloride, barium sulphate is formed, and the presence of sulphur in the gas thus proved.

Estimation of the Total Amount of Sulphur in Coal Gas.—We have long employed a contrivance of Dr. Letheby, which is a most simple and effectual means for estimating sulphur in gas. The objects are to effect the combustion of the gas in a strongly ammoniacal atmosphere, by which means the sulphurous acid is fixed by the ammonia as soon as formed, and to condense the ammonium sulphite. These objects are accomplished in the following way:—After passing the meter, the gas goes through a bottle filled with pebbles moistened with dilute sulphuric acid, for the purpose of estimating any ammonia the gas may contain. The inlet-pipe to this bottle is allowed to pass only 1 inch through the cork; the outlet-pipe passes to the bottom of the bottle. The gas is thus forced through the pebbles from the top, which prevents any accumulation of salt about the inlet-pipe. In place of this bottle, a tube about 6 inches long, $1\frac{1}{2}$ inch in diameter, and drawn out at each end, may be used. It is filled, of course, with pebbles, moistened with sulphuric acid like the bottle, and may be placed horizontally. The gas thus purified from ammonia is consumed at the rate of about half a foot per hour in a Leslie's burner, which is placed under a long funnel-shaped tube. This tube is connected to one end of a large glass cylinder similar to those used for electrical machines, the other end of which is furnished with a piece of glass tube about 4 feet long, joined in such a manner that any products of combustion condensed in it will flow back into the large cylinder.

The means by which ammonia is supplied to the burner are the following:—A wide-mouthed bottle filled with the strongest liquid ammonia is placed immediately beneath the burner, and a funnel, with a short tin tube attached to it, is placed over the bottle in an inverted position. This short tube passes through the centre of the burner, so that the end of it is about 2 inches above the top of the

flame. The draught produced through the whole apparatus, when the burner is alight, is sufficient to evaporate the ammonia in the bottle, which is discharged through the tube into the centre of the receiving tube over the burner, and about 2 inches above the flame. Immediate combination then ensues between the ammonia and the sulphur products of the consumed gas, and the resulting ammonium sulphite is condensed, along with the water formed, in the large cylinder. After pouring out the solution, and rinsing out the cylinder and tubes, the sulphide is converted into ammonium sulphate, and the sulphuric acid estimated as barium sulphate in the usual way.

With this apparatus it is only necessary to observe two precautions—to burn the gas very slowly and to keep up the supply of ammonia. The latter is of the utmost importance.

Mr. Albert Ellissen speaks of this apparatus as follows:—In it the gas is consumed with a Leslie's burner under the best practical conditions for a good oxidation of the sulphur contained in the gas. The consumption with that burner is so slow, that certainly during the ordinary burning of gas so perfect a combustion does not take place, and it may be made similar to the blue flame necessary in heating apparatus—a mode of consumption which should be taken into consideration in the use of gas for domestic purposes. The condensation of the sulphur products (sulphurous and sulphuric acids) in the glass cylinder is complete; experiments having proved that a sensibly greater amount of sulphur is not obtained by increasing the number of those vessels, nor by filling them with ammonia. The apparatus of Dr. Letheby has the additional advantage that the experiments may be made on the average quality of the gas manufactured during the day of 24 hours, and does not require the least superintendence. An interval of a few seconds is sufficient to empty the liquor collected in the cylinder, the quantity of which affords a valuable check on the correctness of the progress of the experiment, and a fresh experiment may be immediately commenced by merely opening the stopcock for the gas.

Valentin's Process for the Estimation of the Total Amount of Sulphur in Coal Gas.—Valentin has found that by passing a mixture of coal gas and air over spongy platinum, and then over a layer of soda-lime, both at a red heat, every trace of the sulphur is absorbed and arrested. He employs a platinum tube, MN, Fig. 16 ($\frac{1}{4}$ size), 18 inches in length, which is heated on a small Hoffmann's combustion-furnace. The portion of the platinum tube marked *a b*, 5 inches in length and $\frac{3}{8}$ ths of an inch in diameter, is charged with a cage constructed of a double roll of fine platinum gauze and filled with spongy platinum. The wider portion of the tube, *b c*, 4 inches in length and $\frac{5}{8}$ ths of an inch in diameter, contains the soda-lime. The air requisite to completely burn the gas enters through a narrow glass tube, connected by means of a small cork at *m* with the

wide end of the platinum tube. A cap of an alloy of silver and copper soldered to this part of the tube strengthens it sufficiently to prevent the thin platinum from being injured by a tightly-fitting cork. The supply of gas to the tube passes through the narrow tube 4 inches long and $\frac{3}{16}$ ths of an inch in diameter, likewise capped, which is seen to branch off at a right angle from the portion of the main tube next to the anterior part of the platinum cage containing the spongy platinum. The products of combustion are allowed to escape at *n*, through the narrow platinum tube, *c n*. Connections for supplying gas and air are made by narrow non-vulcanised black india-rubber tubing.

The air is most conveniently supplied under slight pressure by means of a gas-holder, from which the air is expelled by displacement with water. Such gas-holders are found in most gas-works. A Low's motive-power meter may also be employed with great advantage, as it is capable of being regulated so as to give a supply of air sufficient for one experiment, whilst a small gas-holder would require to be refilled with air once or twice during an experiment. The pressure from the gas-mains is at all times sufficient to send the gas through the platinum

FIG. 16.



tube. The respective proportions of gas and air are best regulated by means of meters, when the pressure-gauge must of course show the same heights of water column; or the air may also be adjusted without having to pass through a meter merely by using a compression-cock on the narrow india-rubber tube.

Preparatory to an experiment the platinum tube is charged with pure soda-lime, by dropping in a lump sufficiently large to easily block up the narrow exit-tube. The whole of the wide portion of the tube, *b c*, is then gradually filled with loose pieces of soda-lime, of a size to enable the operator speedily to shake out the charge of soda-lime when the combustion is over. By gently tapping the platinum tube, held in an upright position whilst it is charged, the layer of soda-lime shakes down pretty completely, and is yet sufficiently porous to allow of a free and easy passage for the gaseous products of the combustion. The cage of spongy platinum is next introduced, and pushed down past the narrow branch tube. The gas and air connections are then made, and the platinum tube is placed upon a small combustion furnace, and heat applied to it from *a* to *c* by turning on the required number of gas-burners at once. The platinum tube is best protected from the action

of the gas-flames by being kept imbedded in asbestos loosely spread in a thin layer along a trough made of tinned sheet iron. The supply of gas to the clay gas-burners should at no time be so great as to cause flames to shoot up above the burners or the tiles which cover the furnace. A dull red heat is sufficient, especially as much heat is generated inside the platinum tube by the combustion of the gas and air within the pores of the spongy platinum.

From 0.5 to 1 cubic foot of gas can conveniently be burned per hour, requiring from 5 to 10 cubic feet of air for its complete combustion. An experiment can thus be done in 3 to 4 hours, since as a rule 2 to 4 cubic feet of gas, burned in the manner described, yield sufficient sulphuric acid for an accurate weighing in the form of barium sulphate.

The experiment over, the tube is allowed to cool in a slow current of air alone. The two ends are disconnected, and the cage of spongy platinum is drawn out by means of a copper wire having a little hook at one end. A stout bit of platinum wire in the form of a loop or ring may also be attached to the cage, for the more ready removal of the platinum cage. The latter is placed into a good-sized test-tube, and treated repeatedly with boiling distilled water, acidulated in the test-tube with a little dilute hydrochloric acid, in order to remove a little sulphuric acid which the spongy platinum retains. The soda-lime is next shaken out into a high beaker, and the tube washed out with hot dilute hydrochloric acid. This is most conveniently done by moving the platinum tube, held in a horizontal position, with its contents of dilute acid backwards and forwards in a small Bunsen gas-flame. The rinsings are poured over the solid soda-lime contained in the beaker. Loss from spirting must be guarded against by rapidly covering the beaker with a large watch-glass after each addition of hydrochloric acid, as long as effervescence takes place. The soda-lime is completely dissolved by the application of gentle heat, and the carbonic acid must be entirely driven off before the sulphuric acid can be precipitated by means of a solution of barium chloride. On gently heating for some time, the precipitate falls down readily and completely, and may be filtered off after standing for a short time, and ignited and weighed as barium sulphate.

The sulphuric acid can also be estimated volumetrically by means of a standard solution of barium chloride.

The following are said by Valentin to be the advantages of this method of estimating sulphur in coal gas :

1. *Perfect* combustion of the gas in a *close* vessel, at a very high temperature.
2. Complete and easy absorption of the sulphuric acid generated by the oxidation of the carbon disulphide, in the *same* vessel in which it was generated.
3. No loss from imperfect condensation.

4. Possibility of completing an experiment in a few hours' time, or, as seems most desirable, during the time of the evening when the greatest consumption of gas occurs.

Carbonic Acid.

Estimation of Carbonic Acid in Natural Water.—M. Lory employs copper phosphate dissolved in a very slight excess of hydrochloric acid. The copper phosphate is obtained by precipitating a solution of copper chloride with ordinary sodium phosphate; the precipitate is collected on a filter, well washed, and, after having been removed from the filter, it is suspended in water and dissolved by the addition of a few drops of hydrochloric acid. When this reagent is added to any water containing alkaline or earthy metals in the state of carbonates or bicarbonates, the result is at first the formation of a bluish-coloured cloudiness, or turbidity. By the addition of a larger quantity of the reagent, this turbidity disappears and the liquid becomes clear again. This point having been reached, the quantity of the reagent employed will be proportional to the total equivalent of the bases present, and consequently to the carbonic acid which was combined with these bases.

In order to titrate the reagent, dissolve 0.265 gramme (equal to $\frac{1}{200}$ of an equivalent) of perfectly pure and dry sodium carbonate in water, and saturate this solution with carbonic acid in order to convert it into bicarbonate; excess of carbonic acid does not at all affect the reagent. 4.4 c.c. of this solution in 1 decilitre of pure water should produce, by the addition of the copper liquor, the reaction already alluded to, and these 4.4 c.c. correspond to 0.22 gramme of carbonic acid.

This reagent is unchangeable and easily prepared, and is effectual no matter what quantity of chlorides, sulphates, &c., be contained in the water; it may even be employed for the alkalimetric estimation of very dilute liquids; but it should be remarked that the reaction is much more exact with bicarbonates than when the bases exist as neutral carbonates or free alkalies. By combining this quick and simple test with the test by the standard solution of soap, both in the natural water and also in the same water after boiling, the most important elements for the appreciation of its ordinary and hygienic qualities will be obtained.

Estimation of Carbonic Acid in Artificial Mineral Waters. In these waters the gas is present under considerable pressure. Mr. H. Napier Draper has devised the following apparatus by means of which the entire quantity of gas is easily and simply estimated.

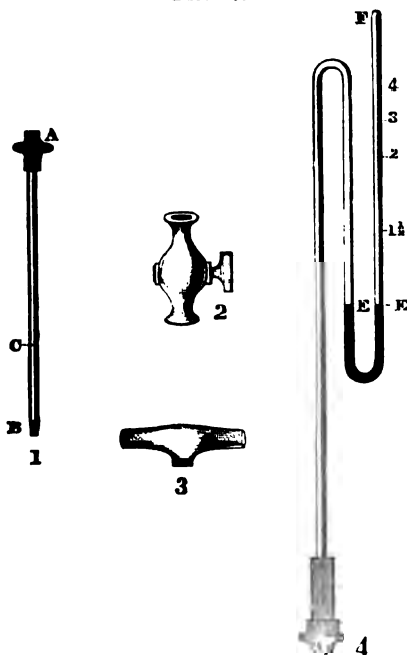
1 is a tube of strong brass furnished at A with a screw, and tipped at B with a sharp steel ferrule. This tube is open at both ends, and is pierced at C with two small holes.

2 is an accurately-ground stopcock, which can be screwed on to A, No. 1.

3 is a handle like that of a gimlet, screwing on to the other end of the stopcock.

4 represents an air-pump syphon-gauge of stout glass tube, securely cemented into a short brass tube, which is also provided with a screw,

FIG. 17.



the thread of which coincides with those of the stopcock and the tube No. 1. Mercury is poured into this tube and adjusted to the level E E'. The space E' F is then graduated, as shown in the figure, by first dividing it into two equal portions and marking the point of division 2. The lower space is then subdivided in the same manner, and the separating line marked $1\frac{1}{2}$. The mark 4 is similarly obtained by dividing the upper space, and the 3 is placed at a point equidistant from 2 to 4.

There are two methods of using this apparatus. The first is more suitable in cases where great accuracy is required; the second is more practically applicable where an approximate knowledge of the gaseous contents of water is required, and

where it is certain that these consist wholly of carbonic acid.

In the first case an ammoniacal solution of barium chloride is prepared by mixing a saturated solution of the salt with half its volume of strong solution of ammonia, and allowing the mixture to become clear by subsidence. The estimation is then proceeded with in the following manner:—A glass flask, capable of holding half as much more fluid as is contained in the bottle experimented upon, is fitted with a cork through which a glass tube passes nearly to the bottom of the flask. About 2 fluid ounces of strong solution of ammonia are now poured into the flask and mixed with 4 ounces of distilled water. The stopcock being adjusted to the tube at A, the handle is now screwed on to the free extremity of the former, and by its aid the steel point is made to penetrate the cork of the bottle to be experimented on until the orifices appear below its under surface. It is used, in fact, precisely as an ordinary cork-borer. The handle is now removed

and the stopcock connected with the glass tube which passes into the flask, by means of a piece of vulcanised tubing about 6 inches long. The stopcock is next turned on just so much as will allow the gas to bubble slowly through the solution of ammonia. The whole is left in this position for 12 hours, by which time all the gas not held in solution at the ordinary pressure will have been absorbed. That which is still retained by the fluid may either be expelled by heating the bottle placed in water, or the entire fluid may be mixed with the contents of the flask.

The carbonic acid can now, of course, be estimated by mixing the solution from the flask with about an ounce of the ammoniacal barium solution above-mentioned, gently heating, separating by filtration, drying and igniting the precipitated barium carbonate as usual. If the whole of the aerated water has been transferred to the flask, and if it contain carbonates or sulphates, or any earthy or metallic base, the weight of these must be deducted from that of the precipitate.

Approximate and Rapid Method of Estimation with this Apparatus. This method of estimation cannot be considered as giving absolutely correct results; but from the facility with which it can be performed, it will be found useful where great accuracy is not required. It must be premised, however, that the necessary correction for temperature must be made; when this is done the results coincide very closely with those obtained by the first-described method.

In this case the stopcock, instead of being connected with the flask, is screwed into the mercury tube, 4, and gradually turned until fully open. Now as water dissolves at the ordinary pressure of 30 inches its own volume of carbonic acid, and as the quantity dissolved at other pressures is directly proportional to the pressure exerted, it is clear that if we know the amount of this pressure and the volume of the water in which the gas is dissolved, we can, knowing also the weight of an equal volume of carbonic acid, estimate by weight the quantity of the latter held in solution. Or, without knowing this latter number, we can express, as is most usual, the quantity of gas in cubic inches. Now it is also clear that as the volume of a gas is inversely as the pressure to which it is subjected, the mercury tube, graduated as in the figure, will show at a glance the number of atmospheres under which the carbonic acid is held dissolved.

Estimation of Carbonic Acid in Solid Carbonates.—Dr. Cameron employs an apparatus shown in Fig. 18. It consists of a light bottle, of the capacity of 75 centimetres. The lower part is divided into two compartments, in one of which the carbonate is placed, in the other the acid. By inclining the bottle, the acid may be allowed to flow over on the carbonate as gradually as the operator pleases. One or two calcium-chloride tubes are inserted through the cork.

The use of anhydrous copper sulphate jointly with fused calcium

chloride is preferable as a drier in case hydrochloric acid is used in the analysis.

Estimation of Carbonic Acid.

Mr. T. S. Gladding uses an apparatus for the estimation of carbonic acid by absorption. It has been used in the author's laboratory for several years, and has proved itself indispensable on account of its great convenience and accuracy.

FIG. 18.



It consists of the ordinary generating flask, followed by an empty U-tube to retain condensed water vapour; this is succeeded by four potash bulbs of the Geissler form. The first of these contains concentrated sulphuric acid to dry the gas. The next two contain potash solution, of sp. gr. 1.27 for absorbing the carbonic acid; the last contains concentrated sulphuric acid to

absorb the moisture taken up from the potash solution. Then comes a U-tube containing soda-lime, and serving as a guard.

The last three Geissler bulbs constitute the weighable portion of the apparatus. Perfectly dry air plus carbonic acid enters these, and perfectly dry air alone escapes. The increase in weight gives the amount of carbonic acid.

The advantages of this apparatus are:—

1. The superiority of concentrated sulphuric acid over calcium chloride as a drying agent on account of (a) its greater thoroughness; (b) its non-absorption of carbonic acid, as is the case with calcium chloride, requiring its previous saturation by a current of the gas; and (c) its greater cleanliness and simplicity of renewal, which takes but a moment, and is necessary only at long intervals.

2. The rapidity with which an analysis may be made. The bubbles of gas may pass at the rate of five per second with perfect safety, and an analysis including all weighings, and a final aspiration of 4 or 5 litres of air, be completed in less than 2 hours.

3. The large quantities of substance that may be used, and the consequent increase of accuracy obtained. 5 grammes of sodium bicarbonate may be used as 1 gramme in the old form, and duplicates easily agree within a few hundredths of a per cent. An analysis of Iceland spar, taking 5 grammes, gave 48.97 per cent.

A strong aspiration must be maintained from the beginning of the analysis, the flow of gas being regulated by a screw clamp placed before the generating flask. 100 c.c. of water are added to the carbonate, and then normal hydrochloric acid to slight excess. Not a trace of hydrochloric acid is carried over on boiling. All the corks are of soft rubber, and black rubber tubing is employed for connections.

BORON.**Detection of Boron in Minerals.**

After estimating the water of crystallisation, Professor Wöhler dissolves the mineral (tinkalcite) in hydrochloric acid, and after neutralising with ammonia, precipitates the calcium with ammonium oxalate, concentrates the filtrate, and estimates the boracic acid in the state of double boron and potassium.

In the case of minerals like tourmaline, which contain fluorine and boron, the question is not so simple. The volatile matters may be estimated by a process analogous to that employed in the case of silicium fluoride, the boron fluoride being changed into a mixture of calcium fluoride and boracic acid. Unfortunately we do not know a method of estimating boron directly in mineral substances, especially if associated with fluorine and silicium; so that if we have boron fluoride, silicium fluoride, and alkaline fluorides, we can estimate the alkalis, but not the boron, silicium, and fluorine. In the absence of a quantitative method for estimating boron, we have an excessively delicate qualitative test. The best method of recognising the presence of boron, if no fluorine is present, is to mix the substance with a small quantity of calcium fluoride and potassium bisulphate, having previously ascertained that the two reagents do not contain boron; two experiments must therefore be made, one on the reagents, and the other on the substance mixed with the reagents. The mixture is slightly moistened, and held on the extremity of a perfectly clean platinum wire. Direct the reducing flame of the blowpipe on to the paste; at the moment when the mixture appears to boil the flame assumes a vivid green colour, characteristic of boron. When but little boron is present, this must not be tried in full daylight, and it should be viewed against a dead black background; the colour of the flame will then be easily detected.

Dr. M. W. Iles finds that borax moistened with glycerine gives before the blowpipe a blue flame which soon changes into a deep green. In subsequent experiments he found it was best first to calcine the mineral, powder, and moisten with sulphuric acid, heat to expel the acid, then to moisten with glycerin and allow to take fire. Thinking that the carbon exerted some action upon the borate, finely-divided charcoal and a borax bead were tried, but they gave negative results.

Glycerin and a sodium carbonate bead gave simply a yellow flame. Various metallic bases in a sodium carbonate bead and glycerin also gave negative results in regard to flame. A 'salt of phosphorus' bead and glycerin gave the light green phosphoric acid flame, but of less intensity than that noticed when a potassium chlorate match is burned. A large number of bases and acids were also experimented upon in

connection with glycerin, using different beads ; also substances treated on charcoal with glycerin, with various results, some of which were without doubt sufficiently characteristic for qualitative reactions.

Estimation of Boracic Acid.

In order to estimate directly the boracic acid contained in datolite, a calcium borosilicate, Professor Wöhler proceeds as follows :—Place the mineral in a small tubulated retort, decompose it with hydrochloric acid, and distil the mixture to dryness ; pour on to the residue the distillate (which contains boracic acid), and allow it to digest to separate the silica. In the liquid precipitate the calcium by means of potassium oxalate, taking care not to add it in too great excess. Then, after filtration and concentration, precipitate the boracic acid in the form of double boron and potassium fluoride. For this purpose add a little potash to the material in a platinum capsule, then pour over the mixture a slight excess of hydrofluoric acid, and evaporate the solution to dryness. To remove the other salts it suffices to treat the mass with a moderately concentrated solution of potassium acetate ; then allow it to digest, and throw on to a filter the double boron and potassium fluoride, and wash it with the same solution of acetate. Then wash with dilute alcohol to remove the potassium acetate. The double fluoride is dried at 100 C., and weighed.

If it be required to estimate boracic acid contained in a solution in which it is contained alone, or in combination with alkaline oxides, A. Ditte proposes to add a little ammonia to the liquid in order to neutralise any free acid, and then an excess of a saturated solution of pure calcium chloride. All the boracic acid is then found as calcium borate, in the form of a gelatinous precipitate, soluble in heat in calcium chloride in excess. The matter introduced into a platinum capsule may then be evaporated to dryness without the least trace of boracic acid being volatilised. When dry, the crucible is filled with a mixture in equal equivalents of pure crystalline sodium and potassium chlorides, and heated moderately at first, and then to fusion. The calcium borate, much less fusible, collects at the bottom of the crucible in a spongy matter more or less agglomerated, and dissolves partially in the melting saline mass. If at the bottom of the crucible a temperature is maintained higher than in the upper part, the dissolved calcium borate crystallises on the surface of the liquid, and forms a ring, which rises along the side of the crucible, just above the surface. Soon all the borax is conveyed into this ring, and nothing remains at the bottom of the crucible. The crystals are insoluble both in hot and cold water. A cold concentrated solution of alkaline chlorides does not affect them ; if hot it dissolves a very small quantity. The matter, when cold, is separated from the crucible, and treated with cold water, when the chlorides dissolve. The crystals are washed on the filter, dried, detached from the filter, and weighed. Care must be taken not to fuse the amorphous

calcium borate which occupies the bottom of the crucible in an early stage of the operation. The temperature of the bottom of the crucible should be kept as high as possible short of such fusion. The crucible cannot be sufficiently heated with a Bunsen burner, but with a gas-lamp. On approaching the point at which the calcium borate is fused, the volatilisation of the alkaline chlorides becomes visible. There should be 1 part of pure dried calcium chloride for 8 parts of the mixture of alkaline chlorides.

Analysis of Borates and Fluoborates.

In solutions which contain only boracic acid and alkalis, Marignac estimates the former as follows:—The solution is neutralised with hydrochloric acid, and magnesium chloride, or preferably the double magnesium or ammonium chloride is added in such quantity that to 1 part of boracic acid at least two parts of magnesia are present. The liquid is now made ammoniacal, and finally is evaporated to dryness in a weighed platinum vessel. Should the addition of ammonia cause a precipitate which does not readily disappear on warming, sal-ammoniac must be added until the liquid becomes clear. During the evaporation it is well to add a few drops of ammonia from time to time. When the mass is dry it is heated to redness, then treated with boiling water; the residue is collected on a filter, and washed with hot water until the washings are not in the slightest degree affected by silver nitrate.

This first residue contains, together with excess of magnesia, the larger part of the boracic acid. A small amount of the latter always goes into solution. The filtrate and washings are treated with ammonia and again evaporated, ignited, and washed as before. The second filtrate and washings are once more treated in the same manner, when great accuracy is required.

The three residues are ignited together in an open crucible as strongly as possible, and sufficiently long to decompose the traces of magnesium chloride which they may contain. When they are weighed, it only remains to estimate the magnesia in them to find by difference the quantity of boracic acid. This can be done either by dissolving in an acid and precipitating magnesium ammonio-phosphate, or more rapidly by dissolving in a known volume of standard sulphuric acid at a boiling heat and estimating the excess of acid by means of a standard alkaline solution.

Should an insoluble, heavy, grey residue remain on treating with acid, it must be collected and its weight deducted from that of the magnesium borate; it will be platinum.

From insoluble compounds the boracic acid is obtained in solution by fusing with three times their weight of sodium carbonate, and exhausting the mass with water. In case of silicates the alkaline solution is digested with ammonium chloride to precipitate silica.

When operating with a fluoborate, the solution of the sodium carbonate fusion is digested with salammoniac to decompose a good proportion, but not all of the sodium carbonate, and is then precipitated with a neutral or ammoniacal solution of calcium chloride. The precipitate of calcium fluoride and carbonate is washed—a matter easily accomplished—dried, gently ignited, treated with acetic acid, evaporated to dryness, and the pure calcium fluoride collected, washed, and weighed. The filtrate, after removing calcium by addition of carbonate and a few drops of ammonium oxalate, may be treated as before described for the estimation of boracic acid.

SILICON.¹

Decomposition of Silicates in the Wet Way.

A. By means of a Fluoride and Acid.—Mr. C. E. Avery finds that silica and silicates, such as felspar and glass, may be completely dissolved in the cold by a mixture of some normal fluoride with almost any of the stronger acids, whether concentrated or dilute.

When mixed with the sodium, barium, aluminium, and lead fluorides, or the double fluorides of these metals, the silicates in question can be readily decomposed by nitric, hydrochloric, or sulphuric acid, either concentrated or diluted with four volumes of water.

If strong sulphuric acid is used, a part of the silicon passes off as gas: if the dilute acid is used, portions of many silicates remain undissolved as insoluble sulphates.

The same decomposition of the silicates is effected, though less easily, by the action of oxalic, acetic, tartaric, and like acids, on the mixed fluoride and silicate. Carbonic acid, even as dilute as it is in the air, does the same thing, but less rapidly.

Strong nitric acid gives a perfect solution and acts rapidly, dissolving a moderately fine powder of felspar or quartz in a few hours, even in the cold. The loss of silica is very slight if the experiment is properly conducted; hence, all the constituents of a siliceous mineral can be estimated in the solution produced.

In analysing the silicates in this way, it is best to use the fluoride of some metal which is not to be estimated in the analysis; since if we use a fluoride whose metal is present in the mineral, we must know the weight of fluoride taken. Of the various fluorides those of barium and lead seem to be the most promising.

An objection to the use of ammonium fluoride is that, as usually made, it contains ammonium sulphate, so that insoluble sulphates might be formed and solution retarded.

If sodium fluoride, as made from cryolite, were not so hard to

¹ For the detection and estimation of silicon in iron and steel see chap. v. p. 168.

purify, it would be well fitted for the analysis of silicates free from sodium.

B. By means of Hydrofluoric Acid.—Professor N. S. Maskeyne employs hydrofluoric acid for the analysis of refractory silicates. The process is conducted in an apparatus of the following construction:—A platinum retort, 80 c.c. in capacity, is fitted with a tubulated stopper of the same material, which reaches nearly to the bottom; a small tube, entering the vertical tube of the stopper at an angle above the neck of the retort, conveys hydrogen to its interior. The vertical tube can be closed, either by a stopper of platinum or by a funnel of that metal, stopped in like manner at the top, and having a fine orifice at its lower extremity.

To the side of the retort, just below its neck, a straight delivery-tube is fixed, which in its turn fits into another platinum tube that, after taking a curve into a vertical position, is enlarged into a cylinder, which passes a considerable distance down a test-tube. The latter, into which the delivery-tube is fitted with a cork, holds 7.5 c.c., or 6.6 grammes of strong ammonia of the sp. gr. 0.88.

The gas delivery-tube inserted in the side of this receiver dips into some more ammonia in a second test-tube.

The pounded mineral, from 0.2 to 0.5 gramme in quantity, and a small platinum ball, are placed in the retort, and the stopper luted to it with gutta-percha, and cemented airtight in its place with caoutchouc and gutta-percha varnish. The funnel, filled with perfectly pure hydrofluoric acid, is now introduced into the tubulure of the stopper, the tap opened, and the acid allowed to run down into the retort. This acid contains about 82 per cent. of absolute hydrofluoric acid—that is to say, a funnel full of this reagent contains 1.12 gramme of acid, capable of rendering gaseous 0.84 gramme of silica, and of neutralising 0.95 gramme of ammonia. The funnel is now replaced by a little platinum stopper, and the orifice secured airtight with gutta-percha varnish. Pure hydrogen is then allowed slowly to traverse the entire apparatus; the retort is placed in a water-bath at 100° C. for two hours, and occasionally slightly shaken to set the ball rotating. During the operation, a trace only of silicon fluoride passes over.

The retort is next transferred to a paraffin bath, and the temperature is cautiously raised. At first hydrofluoric acid passes over, and at this point of the process the flow of hydrogen requires some attention to prevent regurgitation of ammonia. At about 180° C. the silica first becomes visible in fine flocks in the ammonia of the receiver, and in another minute the whole is cloudy.

In eight minutes the rise of the thermometer to 145° C. has brought over so much silicon fluoride that the contents of the tube are semi-solid, and nearly the whole of it has passed over. The temperature is then raised to 150° C., and the retort allowed to cool.

The process is next repeated with a fresh charge of acid and ammonia. If no more than 0.2 gramme of silicate be taken, twice charging of the retort is sufficient; but with 0.5 gramme, three or four repetitions of the process are required. In short, the operation is continued, with fresh reagents, till no more flocks of silica form in the receiver. Finally, 0.75 c.c. of sulphuric acid is introduced into the retort, and the temperature again raised to 160° C., the stream of hydrogen being continued as before.

The several ammoniacal charges are poured into a platinum dish, together with the washings of the delivery-tube and the two test-tubes, and slowly evaporated in a water-bath with continued stirring.

At a point in the evaporation just before the solution becomes neutral and the ammonium fluoride begins to turn acid, the entire silica in the dish will have been dissolved by the fluoride. The process is gradual, but the moment when the solution is complete is easily determined. Then, the dish being removed, potassium chloride is added in slight excess, together with absolute alcohol equal in volume to the contents of the platinum vessel. Potassium fluosilicate precipitates, which, after the lapse of 24 hours, is filtered, washed with a mixture of equal volumes of absolute alcohol and water, dried, and weighed. The results are accurate. In the retort are the bases in the form of sulphates, the treatment of which calls for no further remark.

Decomposition of Silicates in the Dry Way.

For Professor J. Lawrence Smith's process for the decomposition of alkaline silicates, see ante, p. 28.

By Hydrofluoric Acid at a Red Heat.—M. F. Kuhlmann treats silicates at a dull red heat with a current of hydrofluoric acid. The apparatus for this process consists of a platinum retort, of which the body may be of lead; the acid is produced in it by means of sulphuric acid and white cryolite, or pure calcium fluoride. The neck of the retort fits tightly into a tube of platinum, which contains, in boats of the same metal, the matter to be analysed; this tube, by means of a short adapter, also of platinum, communicates with a condensing or absorbing apparatus; this apparatus may be of vulcanised india-rubber. One hour's heating suffices for the treatment of 10 grammes of mineral, but not more than 2 grammes should be employed.

By Fusion with Caustic Alkali.—Mr. Hes heats from 45 to 50 grammes pure potash in a large silver crucible until the mass has assumed a quiet fusion. (Capacity of crucible 70 c.c. water.) Upon the surface of the cooled mass 1 gramme finely powdered silicate is introduced, and the heat is gently applied, increasing the heat towards the end of the fusion, which rarely exceeds 30 minutes. Potassium manganate, silicate, and aluminate will be found, and the iron will remain as sesquioxide; in short, much the same chemical

reactions will ensue as when fusion is made in a platinum crucible with carbonates of the alkalis.

There is, however, a marked difference in the time required for the performance of the process, and the rapidity of the disintegration of the fused mass when treated with water. The lead will not attack the silver crucible in the slightest degree, which is not the case when platinum vessels are used, as has already been indicated.

After the fusion has been completed, the crucible is allowed to cool and is introduced into a vessel containing just sufficient water to cover it, and the mass allowed to dissolve. The silicic acid is then separated as usual. It must be remembered, however, that fused potash or soda will slightly attack silver vessels, and one must take the precaution to wash the silicic acid with some one of the well-known solvents for silver chloride, as strong ammonia or sodium thio-sulphate. This, however, is rapidly and completely performed.

The above mode of procedure has the following advantages:—

1. Rapidity of execution.
2. Complete decomposition.
3. Obviating the use of gas.
4. Replacing the expensive platinum crucibles by less expensive ones.
5. Less liability to loss in the performance of the operation; since by dehydrating the potash before beginning the operation, it then continues quietly to its completion.

Mr. W. Bettell cautions chemists who use the process above given that silver crucibles are seriously attacked. He finds a platinum crucible lined with gold preferable, not merely for this operation, but for oxidation with nitre, fusions with alkaline bisulphates, and fluorides, &c., provided the temperature is below the melting-point of gold.

By Fusion with Baryta.—M. A. Terreil attacks silicates with perfectly pure barium hydrate, fused and pulverised, using 7 to 8 parts to 1 of the silicate. The operation is performed in a silver crucible at 850°, the temperature being raised a little when the fused mass has again solidified, but so as not to reach dull redness. The mass, after cooling, is boiled in pure water in the crucible, and the filtrate is treated with a current of well-washed carbonic acid, raised to a boil, and filtered. The alkalis will be found in the filtrate.

By Fusion with a Fluoride.—Dr. Vorwerk recommends that 1 part of the very finely powdered mineral should be mixed with 3 parts of sodium fluoride, and that this mixture, after having been placed in a platinum crucible, should be covered with 12 parts of powdered potassium bisulphate, and the whole raised to a red heat. Not only are silicates readily decomposed in this manner, but such minerals as chrome-iron ore, red hæmatite, tin ores, rutile, corundum, &c., are very readily brought to fusion and disintegrated by this flux, even with no more heat than that obtained from a good Bunsen gas-burner.

By Fusion with Lead Oxide.—Gaston Bong has proposed to open up silicates with lead oxide, decomposing the unstable compounds formed with nitric acid, and after eliminating the lead by means of sulphuretted hydrogen, proceeding with the analysis in the ordinary manner. This method offers great advantages, since melting lead oxide quickly decomposes the most refractory silicates, even if not in the finest state of mechanical division.

By Fusion with Bismuth Subnitrate.—W. Hempel in conjunction with Dr. Koch has made a number of experiments with this agent, and found it very difficult to prepare a chemically-pure lead oxide. The red lead and the litharge of commerce were found always to contain silica along with other impurities. The preparation of chemically-pure lead oxide from metallic lead by dissolving it in nitric acid and igniting the nitrate thus formed, involves great mechanical difficulties, since the lead nitrate melts before decomposing, and froths strongly, so that small quantities only can be obtained in each operation. All these difficulties are overcome by substituting bismuth oxide for lead oxide, simply igniting the silicate in question with bismuth subnitrate.

This compound is easily obtained in a state of the utmost chemical purity, and it has the further advantage that it does not melt at its temperature of decomposition. The opening up can be performed in the smallest platinum crucibles, as the hyponitric acid liberated fumes slowly away and does not carry with it any of the substance. The resulting melt is dissolved in hydrochloric acid, whilst in the lead process nitric acid is required, which must be afterwards expelled.

Repeated experiments have shown that it is advisable to work with a large excess of bismuth oxide, so as to have a very basic melt, which is easily decomposed by means of hydrochloric acid. The operation succeeds easily if $\frac{1}{2}$ gramme of a silicate is heated gently with 10 grammes of bismuth subnitrate till red fumes no longer escape, and is finally kept in fusion for about ten minutes. The melt is poured as far as possible whilst still liquid into a platinum capsule floating upon cold water, and the mass thus obtained and the crucible are treated with concentrated hydrochloric acid. The solution thus obtained is evaporated to dryness for the elimination of silica; the residue is taken up with hydrochloric acid; the silica filtered off and washed with water acidulated with hydrochloric acid.

On diluting the filtrate with water the greater part of the bismuth is precipitated as oxychloride. It is filtered off, washed, and from this second filtrate the remainder of the bismuth is precipitated by means of sulphuretted hydrogen. The further treatment of the filtrate is effected in the ordinary manner.

In order to throw a light upon a possible error due to the volatilisation of the alkalis at the melting temperature of bismuth oxide, a felspar was decomposed by this method, and by the hydrofluoric process. The results were :—

With bismuth—

Potash	7.60,	7.70
Soda	4.71,	4.72

With hydrofluoric acid—

Potash	7.86,	7.77
Soda	4.70,	4.84

The operation can be safely conducted in a platinum crucible if care be taken that it is not in a reducing atmosphere. If reducing gases are present, metallic bismuth is formed, which destroys the crucible. Silicates which contain organic matter must first be ignited with access of air. A number of meltings have been performed in the same crucible, which suffered no injury.

As bismuth is a costly metal it is prudent to work up all the precipitates into subnitrate. This may be conveniently done by melting the residues and the filters along with soda in a Hessian crucible, dissolving in nitric acid the metallic bismuth thus obtained, and precipitating the solution with water as a basic nitrate.

The decomposition of silicates should be effected under a draught, as the bismuth oxidises slightly at the melting-point, and the vapours seem to be very poisonous.

Separation of Silica in the Analysis of Limestones, Iron Ores, &c.—The mineral is decomposed by hydrochloric acid, evaporated to dryness, and then treated with hydrochloric acid and water. Silica in the insoluble condition, and the bases as soluble chlorides, are thus obtained, and these are separated by filtration.

Many silicates, however, do not yield to this treatment, prominent among them being clay. This aluminium silicate is hardly ever absent as a more or less intimate admixture in such samples of limestones, iron, and manganese ores, and other minerals, as occur for manufacturing processes. Consequently, if silica be present in the form of clay, or any other non-decomposable silicate, the insoluble residue referred to above is not pure silica, but contains alumina or other bodies. Dr. Percy, in the analyses of British iron ores which were made in his laboratory, and are given in his 'Metallurgy of Iron,' examined separately the soluble and the insoluble part of the samples. On referring to these tables, it will be found that the insoluble residue is, with one exception, never pure silica, but contains alumina, and mostly also other bases. If the quantity of insoluble substance be small, say below 2 per cent., and iron and certain rarer bodies are known to be absent, we may safely, unless absolute accuracy is required, treat it with hydrofluoric and sulphuric acids, ignite, and assume the difference to be silica, the residue being alumina. If the appearance of the insoluble matter be that of pure quartz, we may take it to be all silica.

For more accurate analysis, however, and when the insoluble resi-

due is considerable in quantity, either the whole of the sample under treatment, or the insoluble part, must be fused with sodium carbonate, or some other basic flux, in order to obtain a more basic compound, which is readily decomposed by hydrochloric acid. This way of proceeding has two drawbacks, which, whenever possible, are eschewed by the analyst, viz. considerable expenditure of time, and the introduction of a considerable quantity of foreign matter into the substance under examination.

Mr. H. Rocholl proposes to utilise as flux the bases present in the mineral itself. He prepares by mere ignition, a basic silicate decomposable by hydrochloric acid.

As regards *limestones*, specimens have been successfully treated containing up to 21.2 per cent. silica and 6.5 alumina, care being taken to prove the purity of the silica obtained. In this case the same portion of the finely-powdered sample which has served for the estimation of water and carbonic acid by ignition in a platinum crucible is utilised. It is transferred into a dry basin, and carefully treated with a little water; the lime left in the crucible is then washed into the basin with water and hydrochloric acid, and more acid is added until solution has taken place. The evaporation to dryness is then quickly effected, as only small quantities of liquid have to be employed. The silica obtained is perfectly pure.

For the analysis of *ores* a somewhat more circuitous procedure is necessary, as the sample after ignition has to be re-weighed and re-powdered. Weigh out into a tared platinum crucible a quantity of the finely-powdered sample, something more than what is required for actual analysis: then ignite, at first gently, afterwards for about 20 minutes, to nearly a white heat, either on a good muffle or within a clay jacket over a strong blowpipe flame. An incipient fusion should take place. Weigh and carefully detach as much as possible from the crucible: this will be effected easily if the substance before ignition had been pressed into one corner of the crucible, and not spread over the bottom. The mass will be found exceedingly hard, and is best treated by being at first roughly powdered in a steel mortar and then finished in an agate or wedgewood mortar.

In weighing out a portion for analysis, an allowance may be made in proportion to the loss sustained in the ignition, so that subsequently calculations may be made on the weight usually taken for analysis. The powder is then digested in a porcelain dish with strong hydrochloric acid. If the treatment has been successful, a clear jelly or solution will readily form, and the analysis can be proceeded with in the ordinary way.

The ignited silica may still contain certain impurities in small quantities. Titanic acid has to be looked for in certain iron ores, and barium sulphate in manganiferous ores; indeed, Mr. H. Rocholl says he has met with a red hematite which contained 19 per cent. of the

latter body. It is advisable, in the presence of baryta, to precipitate it completely as sulphate before filtering the silica. The ignited residue, on treatment with hydrofluoric and sulphuric acids, will leave the whole of it, the difference being silica. The residue may be examined for titanitic acid by the known methods.

The applicability of this method is limited by the percentage of silica. It was successful with ores containing up to 25 per cent. silica, but not with an ore containing 81 per cent. The latter was a magnetic ore, containing 41 per cent. of iron; the gangue consisted of quartz, greenstone, and garnet. In order to try if the want of success was merely owing to the excessive amount of silica, and not to the nature of the compounds in which it occurred, to a fresh portion 50 per cent. of ferric oxide was added, so bringing the silica down to about 21 per cent. After ignition, a mass was obtained which was readily decomposed, even in rough lumps.

Calcined Cleveland mine, a very heterogeneous mixture of numerous compounds, which does not even yield the whole of its iron to hydrochloric acid, is readily decomposed after semi-fusion of the finely-powdered sample.

The platinum crucible, after use, is best cleaned by fusing some sodium carbonate in it. Although hydrochloric acid slowly dissolves whatever adheres to the sides, its use is better avoided on account of the possible presence of manganese.

The idea of letting the base contained in the mineral act as a flux for its impurities seems so readily to suggest itself, that other chemists may have been employing it, particularly for limestones, where its advantages are greatest.

Estimation of Ferrous Oxide in Silicates.—W. Earl proceeds as follows :—

About 2 grammes of the finely-powdered mineral are placed in a deep platinum crucible, and 40 c.c. of hydrofluoric acid (containing about 20 per cent.) are added. The whole is heated to near the boiling-point, and occasionally stirred with a platinum wire until the disintegration of the silicate is complete, which usually takes place in about ten minutes. 10 c.c. of sulphuric acid diluted with an equal volume of water are now added, and the heat is continued for a few minutes. The crucible and its contents are then quickly cooled, diluted with water which has been freed from oxygen by previous boiling, and the ferrous salt present is estimated by titration with potassium permanganate or bichromate.

It may be remarked that hydrofluoric acid which has been prepared in a leaden vessel invariably contains sulphurous acid. In order to render such acid fit for use, potassium permanganate must be added until the colour just ceases to be discharged.

In the analysis of a large number of trap-rocks, it was found that in every case a far larger percentage of ferrous oxide was obtained by

dissolving the mineral in hydrofluoric acid, than by fluxing it with sodium and potassium carbonate.

Thus, in the analysis of a trap-rock which contained 1.2 per cent. of manganous oxide, 5.78 per cent. of ferrous oxide was obtained by solution in hydrofluoric acid, whereas the method of fluxing only yielded 1.8 per cent.

W. Knop gives the following method for separating the alkalis in silicates from ferric oxide, alumina, lime, and magnesia.

If in dissolving a siliceous mineral we employ a mixture of $\frac{1}{3}$ fuming hydrochloric acid and $\frac{2}{3}$ hydrofluoric acid, everything dissolves during evaporation to a clear liquid, but on further concentration hydrochloric acid escapes, and the alkaline silicofluorides reappear along with the iron, aluminium, calcium, and magnesium chlorides.

If a silicate contains a quantity of silica equal to its proportion of alkaline metals, or if, supposing the silica to be insufficient or totally wanting, we dissolve the substance in 10 to 20 c.c. of water, and a few c.c. of hydrochloric acid and add a corresponding quantity of silica, we can convert its alkali metals completely into silicofluorides, by adding the requisite quantity of fuming hydrofluoric acid and evaporating.

The alkaline silicofluorides are absolutely insoluble in a mixture of ether and absolute alcohol strongly acidified with hydrochloric acid. Hence the alkaline silicofluorides may be precipitated from a hydrochloric solution in the form of a crystalline deposit by the addition of ether and absolute alcohol. But if the hydrochloric solution contains also iron, aluminium, calcium, and magnesium chlorides, the alkaline silicofluorides are deposited, not in a pure state, but in combination with small quantities of the above-mentioned metals, the bulk of which, however, remain in solution as chlorides.

The process is carried out as follows:—The weighed substance is mixed in a platinum crucible with a few c.c. of water, and in case of need with a corresponding quantity of silica. A sufficiency of hydrofluoric acid is then added and all the liquid is evaporated off. The dry residue is covered with 2 to 3 c.c. of fuming hydrochloric acid, upon which it is readily detached from the crucible. It is washed into a beaker by means of an alcohol washing-bottle, using 25 or at most 50 c.c. of absolute alcohol for washing out the crucible; the acid liquid is allowed to act for some time upon the precipitate. 100 c.c. of ether are then added, and the whole is allowed to stand for 12 hours.

The ethereal liquid is poured off from the precipitate, and the alkaline silicofluorides are brought upon a filter by means of an alcohol washing-bottle. The use of a feather is admissible only at the beginning; a glass rod is objectionable because it makes the precipitate adhere again to the inside of the glass. The precipitate may be transferred easily if the beaker is held in a sloping position over the filter, and a few c.c. of alcohol are ejected behind the precipitate so as to wash it into the filter.

The filter is then washed slightly with alcohol, so as to remove the ether; it is then dried, the precipitate removed, the paper is burnt completely in a platinum capsule; the precipitate is added to the ash, mixed with concentrated sulphuric acid, allowed to stand for some time until the silicofluoric gas has chiefly escaped, and then ignited so long and at so low a temperature that the alkalies may remain behind as acid sulphates and be unable to react upon the silica liberated.

The residue in the capsule is drenched with 10 to 20 c.c. of ammonia and evaporated to dryness, or at least to a paste-like condition. The mass takes again an acid condition by the loss of ammonia, and strong ammonia is therefore added drop by drop until the reaction is again alkaline. The mixture is then allowed to stand for an hour to allow of the complete separation of the ferric oxide and the alumina. Upon the pasty mass is then poured about 20 c.c. of a solution of ammonium monocarbonate (prepared by mixing 180 c.c. ammonia, sp. gr. 0.92, with 230 grammes ammonium sesquicarbonate and water enough to make up 1 litre), and allowed to stand for 12 hours in the covered platinum capsule.

The quantities of ferric oxide, alumina, lime, and magnesia thus separated are so small that the entire precipitate may be collected upon a very small filter. It is washed with the smallest possible quantity of the above-mentioned ammonium carbonate.

The filtrate is now exposed first for some time to a very gentle heat, a quantity of ammonium bitartrate corresponding to the ammonium sulphate present in the solution is added, the liquid is evaporated to dryness, and the residue is heated for some time in the air-bath to a temperature above 100°. The object of adding ammonium bitartrate is to prevent spirting during the ignition of the ammonium sulphate. The residue is ignited till perfectly white, and weighed. It is then redissolved in hot water, mixed with 2 to 3 drops of the solution of ammonium monocarbonate, and set aside to see if any further deposit of iron oxide and alumina takes place.

If this is the case the liquid is again evaporated to dryness. These supplemental deposits generally attach themselves so firmly to the platinum that a clear solution is obtained on drenching the residue with 10 to 20 c.c. of boiling water. This solution is decanted into a second platinum capsule in which the solution is evaporated to dryness and the capsule is again strongly ignited and weighed. It is recommended to add a few drops of sulphuric acid during this second evaporation.

Separation of Crystalline Silicic Acid, especially Quartz, when mixed with Silicates.—E. Laufer takes advantage of the property of phosphorus salt to dissolve metallic oxides at a melting heat, and to isolate silicic acid from silicates without attacking quartz. To the finely-powdered material weighed in a platinum capsule, phosphorus salt is added in a larger quantity than is required for the

solution of the silicates supposed to be present, the crucible not being more than half full. It is gradually and cautiously heated in the air-bath, then melted, the heat being finally urged with the blast till the mixture is in tranquil fusion. The cold mass is easily separated from the crucible, and is then boiled for a length of time with dilute hydrochloric acid, washed by decantation, and filtered, the silicic acid being then extracted from the residue with boiling soda.

Estimation of Clay in Arable Soils.—Th. Schloësing states that the separation of clay, sand, and calcareous matter by levigation is deceptive, since the last lot, supposed to contain the clay, includes in reality whatever is of extreme tenuity, whether sand, lime, or true clay. Two soils which give the same result by levigation may be exceedingly unlike if the last lot in the one consists of clay, and in the other of a mixture in which an extremely fine sand predominates. The author takes a sample of 5 grammes, previously freed from stones and organic matter, made up into a paste with a little water, and rubbed up with the finger in a capsule. More and more water is gradually added, and the suspended matter is poured off. By constantly adding water and rubbing, nothing remains in the capsule but sand, which is rubbed until it yields nothing more to water, and is then thrown into the vessel in which all the washings and decantations have been united. The coarse sand is now separated in the ordinary manner by decantation and washing, dried, weighed, and the calcareous sand and organic particles estimated in the ordinary manner. The fine sand, calcareous matter, and clay are now found suspended in 800 or 400 c.c. of water. Nitric acid is now added in small successive quantities, stirring repeatedly on each addition until the lime is dissolved and the liquid remains clear. The clay is, in fact, coagulated by the calcium salts formed, but the same clearness is noticed when the soil is quite deprived of calcareous matter. It is due to the presence of free acid.

Traces of hydrochloric, nitric, or sulphuric acid have the power of coagulating clay as decidedly as calcium or magnesium salts. After this treatment with acid, the mixture of clay and fine sand is filtered and washed. As soon as the calcareous salts and the free acid are eliminated, the filtrate passes turbid, and filtration becomes difficult. The clay has then resumed its property of diffusion in pure water. The whole is then washed out of the filter into a precipitating-glass of 2 litres capacity. The amount of water consumed in washing the filter clean is, at most, 150 litres. Upon the mixture we pour 1 to 2 c.c. of liquid ammonia and digest for 1 hour. The glass is then filled up with pure water, stirred, and set aside for 24 hours. After this time the amount of fine sand remaining suspended is unimportant. The clay-liquid may be then drawn off by means of a syphon. The residue is washed into a capsule, weighed, and dried. It is fine sand, but is generally confounded with clay. On its surface there is generally found a brown coating, which contracts as it dries and separates from

the sand. It consists of organic matter rich in iron oxide. The argillaceous liquid is coloured by a compound ammonium, iron and aluminium humate. On neutralising the ammonia and acidifying slightly, the clay and the organic matter fall together. To separate these two colloids as far as possible, a few grammes of sal-ammoniac are dissolved in the alkaline liquid. The clay coagulates whilst the humate remains suspended. When the liquid has become clarified by standing, it is decanted as far as possible; the rest, along with the clay, is thrown on a tared filter, dried at 100°, and washed.

CHAPTER XIV.

GENERAL ANALYTICAL PROCESSES.

GAS ANALYSIS.¹**Analysis of a Mixture of Oxygen, Carbonic Acid, and Nitrogen.**

1. **INTRODUCE** a portion of the mixture into a graduated tube over mercury, and note accurately the volume.

To estimate the carbonic acid, pass into the tube, by means of a curved pipette, a small quantity of a concentrated solution of potash, and agitate several times until there is no further variation in the level of the liquid; the carbonic acid will be absorbed by the potash. To obtain the volume very accurately, transfer the gas to a vessel of water so as to allow the alkali to fall out; then retransfer the gas to another tube and estimate its volume, saturated with moisture.

To estimate the oxygen, first introduce into the tube a concentrated solution of potash, then a little pyrogalllic acid. Upon agitation, the oxygen is absorbed, and the nitrogen remains. The bulk of the latter gas may be obtained by taking the same precautions as in the former instance.

After having removed the carbonic acid, phosphorus may also be employed to absorb the oxygen. The experiment may be performed in two ways:

a. In the Cold.—In the tube containing the gas (over mercury) pass up a long stick of moist phosphorus, the sides of the tube being at the same time moistened. The oxygen combines with the phosphorus, giving phosphorous acid, which dissolves in the water. At the end of an hour the absorption is completed. It may be known by the absence of white fumes on the stick of phosphorus. Remove the latter, dry the gas, and measure its volume; it will be nitrogen.

b. With Heat.—The analysis is effected much more rapidly in the following manner:—In a curved tube containing the mixture of oxygen and nitrogen standing over water, introduce by means of an iron wire a small piece of phosphorus, so that it rests in the upper curved portion of the tube; then remove the iron wire and heat the phosphorus, at

¹ These methods are principally founded on instructions given by Drs. Grandeau and Troost.

first carefully, to volatilise the water which remains in the bend of the tube, and then rapidly, so as to inflame the vapour of phosphorus. A greenish flame will be seen to advance, gradually absorbing the oxygen of the air. When it has descended to the level of the liquid it disappears, and the experiment is terminated. Allow it to cool, and estimate the volume of the residual nitrogen.

2. The analysis of a mixture of carbonic acid, oxygen, and nitrogen may be effected with a little more accuracy in the following manner:—The dry mixture being contained in a graduated tube standing over mercury, introduce a piece of caustic potash fixed to the extremity of a platinum wire, and slightly moistened. When the carbonic acid is absorbed, withdraw the piece of potash, and a simple observation gives the residual volume of the mixed oxygen and nitrogen perfectly dry.

The residue is introduced into a mercurial eudiometer. Add to the mixture double its volume of hydrogen, and pass the electric spark. Water will be produced by the combination of the hydrogen and oxygen in the proportion of 2 volumes of the former to 1 volume of the latter. One-third of the diminution in volume, therefore, represents the volume of oxygen. The volume of nitrogen is obtained by difference; it will be the excess of the original volume of the mixture over the sum of the volumes of oxygen and carbonic acid.

The estimation of oxygen by the eudiometer is not exact unless this gas is present in tolerable quantity in the mixture. If there is only a very small proportion, it is necessary, in order to ensure complete combustion, to take the precaution to introduce into the mixture a sufficiently large quantity of oxyhydrogen gas, obtained by decomposing acidulated water with 8 or 4 Bunsen's elements. The gas should be passed through concentrated sulphuric acid in order to dry it.

8. For the estimation of oxygen in the gases escaping from the lead chambers Vogt uses an apparatus by which a known volume of the gas is collected after passing through a solution of potassium chromate and caustic lye contained in Liebig's bulb-tubes. He then adds to the gas a solution of ammonium-ferrous sulphate and ammonia enough to throw down all the ferrous oxide, by which the oxygen of the gaseous mixture is entirely absorbed. Water is then allowed to re-enter the apparatus when the quantity absorbed indicates the volume of oxygen which has disappeared. Or the precipitate of oxide may be redissolved in sulphuric acid and titrated with permanganate. The apparatus consists of an aspirator flask filled with water recently boiled. This aspirator is connected with the gas to be examined and the water is allowed to escape. The apparatus is filled with the gas, which has been previously freed by a passage through the bulb-tubes from all gases except oxygen and nitrogen. There is a tube with a tap fixed to the flask for the introduction of the reagents.

Mixture of Oxygen, Hydrogen, and Nitrogen.

1. After having measured the volume of the mixture, absorb the oxygen by potash and pyrogallic acid, or by phosphorus, as already described at p. 686.

Pass the remainder into a curved tube over mercury, and introduce into it a piece of compact copper oxide,¹ and heat it for about 20 minutes; all the hydrogen is then absorbed; the residue will be nitrogen; it may be transferred to a graduated tube, and its volume measured.

After the absorption of the oxygen the hydrogen may be estimated by introducing it into the eudiometer with half its volume of oxygen. Two-thirds of the diminution of volume occasioned by the passage of the spark represents the volume of hydrogen. The nitrogen is given by difference.

2. The analysis may also be effected entirely by the eudiometer. Introduce the original mixture into the eudiometer, with twice its volume of hydrogen, and pass the spark. The volume of hydrogen which enters into combination will be two-thirds the diminution of volume, the oxygen being represented by the other third. This first experiment will therefore give the amount of oxygen. In order to ascertain the amount of hydrogen in the mixture, add to the residue of the first explosion half its volume of oxygen, and pass the spark a second time. Two-thirds of the diminution of volume will be hydrogen. The excess of the sum of the volumes of hydrogen burnt in these two experiments over the volume of this gas introduced into the eudiometer represents the volume of hydrogen found in the original mixture. The nitrogen will still be given by difference.

Mixture of Hydrogen, Marsh Gas, and Nitrogen.

Introduce the mixture into a mercurial eudiometer, with twice its volume of oxygen, and pass the spark. The free hydrogen and that in the marsh gas combine with the oxygen to form aqueous vapour, which condenses. The carbon becomes carbonic acid. The residue is therefore a mixture of nitrogen, oxygen, and carbonic acid.

Pass these gases into a graduated tube, and after having observed the volume, absorb the carbonic acid with potash. The diminution of volume gives the volume of carbonic acid, which will be equal to the volume of the carburetted hydrogen originally present.

If a little pyrogallic acid is then introduced into the potash, the rest of the oxygen is absorbed, and the volume of nitrogen is obtained as a residue.

¹ This oxide is prepared by fusing two parts of copper oxide with one part of lead oxide. The fused mass is run on to a plate of copper, then broken into pieces and preserved in bottles.

The amount of the hydrogen which existed in the free state in the original mixture is obtained by taking the excess of the volume of the original mixture over the sum of the volumes of nitrogen and marsh gas.

**Mixture of Sulphuretted Hydrogen, Carbonic Acid,
and Nitrogen.**

The mixture is measured into a graduated tube standing over mercury. Introduce a solution of copper sulphate and agitate. The diminution of volume represents the amount of sulphuretted hydrogen present.

Bunsen recommends in preference for the absorption of the sulphuretted hydrogen a ball of manganese binoxide impregnated with phosphoric acid. [To obtain a ball of manganese binoxide which does not tend by reason of its porosity to absorb other gases besides sulphuretted hydrogen, Bunsen prepares by levigation a fine powder, which is formed into a thick paste by a little water. This paste is then pressed into a mould round a platinum wire, the extremity of which is twisted into a spiral. The mould is then dried at a gentle heat, when the ball of binoxide is readily detached; for greater precaution, the sides of the mould may be smeared with a little oil. The ball is then moistened several times with a syrupy solution of phosphoric acid.]

The remaining gas, transferred to an appropriate tube, is then submitted to the action of caustic potash, which absorbs the carbonic acid. The residue is nitrogen.

**Mixture of Hydrochloric Acid, Sulphuretted Hydrogen,
Carbonic Acid, and Nitrogen.**

When the exact volume of the mixture has been measured in a tube over the mercury, the hydrochloric acid is absorbed by a fragment of hydrated sodium sulphate fixed to the extremity of a platinum wire. [To obtain these fragments fuse ordinary sodium sulphate in its water of crystallisation, and dip in several times the end of the platinum wire. There adheres to the wire a small lump of the sulphate, which augments in volume with each fresh immersion.]

Then remove the sodium sulphate and measure the volume again. The diminution observed will represent the volume of hydrochloric acid gas.

The sulphuretted hydrogen is absorbed by a ball of manganese binoxide soaked in phosphoric acid, and the carbonic acid is afterwards absorbed by potash. The residue gives the nitrogen.

Mixture of Sulphurous Acid, Carbonic Acid, Oxygen, and Nitrogen.

(Gas issuing from Craters of Solfataras.)

The volume of the mixture being measured dry in a graduated tube over mercury, the sulphurous acid is absorbed by a ball of manganese binoxide, impregnated with phosphoric acid. After having removed this ball and noted the diminution of volume, a fragment of potash is introduced to absorb the carbonic acid. The second diminution of volume will give the carbonic acid.

The oxygen can then be absorbed by potash and pyrogallie acid, or it may be estimated eudiometrically, as described at p. 636. The nitrogen will remain as residue.

Sulphuretted Hydrogen, Carbonic Acid, Hydrogen, and Nitrogen.

(Fumeroles of Volcanoes.)

Commence by absorbing the sulphuretted hydrogen by introducing into the mixture a ball of manganese binoxide impregnated with phosphoric acid. The absorption of the carbonic acid is then effected by means of a fragment of moist caustic potash.

The hydrogen is then estimated as at p. 638, either by the eudiometer, or by passing the mixture of hydrogen and nitrogen into a curved tube and introducing compact copper oxide into the upper part of the bend. By heating the part of the tube containing this oxide for a quarter of an hour, the complete absorption of the hydrogen is effected. The nitrogen will form the residue.

Carbonic Acid, Carbonic Oxide, Hydrogen, and Nitrogen.

(Gas from Blast Furnaces where Wood is used.)

After having accurately measured the volume of the mixture over mercury, absorb the carbonic acid with a fragment of caustic potash.

Then estimate the carbonic oxide by introducing into the graduated tube a solution of copper subchloride in hydrochloric acid, agitate, and the absorption will be complete.

Instead of introducing the liquid itself, it will be better, as Bunsen advises, to introduce a ball of papier-maché impregnated with this acid solution of copper subchloride.

This experiment should be made over another separate mercurial trough, for the copper subchloride attacks and fouls the mercury.

In withdrawing the ball impregnated with chloride, before reading off the volume, it is necessary to remove the hydrochloric acid vapours given off by the chloride.

The estimation of the hydrogen can then be effected as already described, either by the eudiometer or by absorption with copper oxide. The nitrogen remains as a residue.

**Carbonic Acid, Carbonic Oxide, Hydrogen, Marsh Gas,
and Nitrogen.**

(Gas from the Mud of a Pond.)

First estimate the carbonic acid by means of potash, then with a ball of papier-maché introduce into the mixture a concentrated solution of copper subchloride in hydrochloric acid. After the absorption has terminated, withdraw the ball of chloride and replace it by a ball of potash to remove the vapours of hydrochloric acid given off by the acid chloride. If the mixture which contains carbonic oxide also contains oxygen, the latter gas is estimated first by pyrogallic acid and potash. The estimation of the hydrogen and marsh gas is then effected eudiometrically, as already shown at p. 638.

**Sulphuretted Hydrogen, Carbonic Acid, Carbonic Oxide,
Olefiant Gas, Marsh Gas, Hydrogen, and Nitrogen.**

(Coal Gas.)

The mixture is first accurately measured in a graduated tube standing over mercury. The sulphuretted hydrogen is then estimated by means of a ball of manganese binoxide impregnated with phosphoric acid.

After removing the manganese binoxide and measuring the remaining volume, introduce a ball of caustic potash, which absorbs carbonic acid.

The carbonic oxide is estimated by means of acid copper subchloride.

To estimate the olefiant gas introduce into the residue a fragment of coke soaked in a concentrated solution of anhydrous sulphuric acid in monohydrated sulphuric acid. The absorption of the olefiant gas takes place very rapidly; the coke is then withdrawn and the acid vapours absorbed by potash.

The estimation of the hydrogen and marsh gas is then performed as described at p. 638. The nitrogen remains as a residue.

The olefiant gas, as well as the marsh gas and the hydrogen, may also be estimated by the eudiometer. To effect this pass the mixture of these three gases and the nitrogen into the eudiometer with three times its volume of oxygen, and pass the spark. The free hydrogen, as well as that of the carburets, combines with oxygen to form water, whilst the carbon becomes carbonic acid. Then pass the residue of the combustion into a graduated tube, and estimate the carbonic acid with potash, and the excess of oxygen with potash and pyrogallic

Mixture of Sulphurous Acid, Carbonic Acid, Oxygen, and Nitrogen.

(Gas issuing from Craters of Solfataras.)

The volume of the mixture being measured dry in a graduated tube over mercury, the sulphurous acid is absorbed by a ball of manganese binocide, impregnated with phosphoric acid. After having removed this ball and noted the diminution of volume, a fragment of potash is introduced to absorb the carbonic acid. The second diminution of volume will give the carbonic acid.

The oxygen can then be absorbed by potash and pyrogallic acid, or it may be estimated eudiometrically, as described at p. 636. The nitrogen will remain as residue.

Sulphuretted Hydrogen, Carbonic Acid, Hydrogen, and Nitrogen.

(Fumeroles of Volcanoes.)

Commence by absorbing the sulphuretted hydrogen by introducing into the mixture a ball of manganese binocide impregnated with phosphoric acid. The absorption of the carbonic acid is then effected by means of a fragment of moist caustic potash.

The hydrogen is then estimated as at p. 638, either by the eudiometer, or by passing the mixture of hydrogen and nitrogen into a curved tube and introducing compact copper oxide into the upper part of the bend. By heating the part of the tube containing this oxide for a quarter of an hour, the complete absorption of the hydrogen is effected. The nitrogen will form the residue.

Carbonic Acid, Carbonic Oxide, Hydrogen, and Nitrogen.

(Gas from Blast Furnaces where Wood is used.)

After having accurately measured the volume of the mixture over mercury, absorb the carbonic acid with a fragment of caustic potash.

Then estimate the carbonic oxide by introducing into the graduated tube a solution of copper subchloride in hydrochloric acid, agitate, and the absorption will be complete.

Instead of introducing the liquid itself, it will be better, as Bunsen advises, to introduce a ball of papier-maché impregnated with this acid solution of copper subchloride.

This experiment should be made over another separate mercurial trough, for the copper subchloride attacks and fouls the mercury.

In withdrawing the ball impregnated with chloride, before reading off the volume, it is necessary to remove the hydrochloric acid vapours given off by the chloride.

The estimation of the hydrogen can then be effected as already described, either by the eudiometer or by absorption with copper oxide. The nitrogen remains as a residue.

**Carbonic Acid, Carbonic Oxide, Hydrogen, Marsh Gas,
and Nitrogen.**

(Gas from the Mud of a Pond.)

First estimate the carbonic acid by means of potash, then with a ball of papier-maché introduce into the mixture a concentrated solution of copper subchloride in hydrochloric acid. After the absorption has terminated, withdraw the ball of chloride and replace it by a ball of potash to remove the vapours of hydrochloric acid given off by the acid chloride. If the mixture which contains carbonic oxide also contains oxygen, the latter gas is estimated first by pyrogallie acid and potash. The estimation of the hydrogen and marsh gas is then effected eudiometrically, as already shown at p. 638.

**Sulphuretted Hydrogen, Carbonic Acid, Carbonic Oxide,
Olefiant Gas, Marsh Gas, Hydrogen, and Nitrogen.**

(Coal Gas.)

The mixture is first accurately measured in a graduated tube standing over mercury. The sulphuretted hydrogen is then estimated by means of a ball of manganese binoxide impregnated with phosphoric acid.

After removing the manganese binoxide and measuring the remaining volume, introduce a ball of caustic potash, which absorbs carbonic acid.

The carbonic oxide is estimated by means of acid copper subchloride.

To estimate the olefiant gas introduce into the residue a fragment of coke soaked in a concentrated solution of anhydrous sulphuric acid in monohydrated sulphuric acid. The absorption of the olefiant gas takes place very rapidly; the coke is then withdrawn and the acid vapours absorbed by potash.

The estimation of the hydrogen and marsh gas is then performed as described at p. 638. The nitrogen remains as a residue.

The olefiant gas, as well as the marsh gas and the hydrogen, may also be estimated by the eudiometer. To effect this pass the mixture of these three gases and the nitrogen into the eudiometer with three times its volume of oxygen, and pass the spark. The free hydrogen, as well as that of the carburets, combines with oxygen to form water, whilst the carbon becomes carbonic acid. Then pass the residue of the combustion into a graduated tube, and estimate the carbonic acid with potash, and the excess of oxygen with potash and pyrogallie

acid. The residue left after this double absorption gives the nitrogen.

The volumes of olefiant gas, marsh gas, and hydrogen may then be obtained by a simple calculation. The reactions which take place show:—1. That the combustion of olefiant gas requires thrice its volume of oxygen, that of marsh gas double its volume, and that of hydrogen half only. 2. That the olefiant gas produces double its volume of carbonic acid, and the marsh gas its own volume exactly.

Therefore, calling x , y , z the volumes of the olefiant gas, the marsh gas, and the free hydrogen, of which the sum is known and represented by c , we have—

$$\begin{aligned} 3x + 2y + \frac{z}{2} &= a \\ 2x + y &= b \\ x + y + z &= c \end{aligned}$$

a and b are the volumes of oxygen employed, and of the carbonic acid produced—volumes which have been determined by experiment.

To find the values of x , y , and z , subtracting the first equation from the sum of the two others, we find—

$$\frac{z}{2} = c + b - a; \text{ whence } z = 2(b + c - a).$$

Then subtracting the last from the second, we find—

$$x - 2(b + c - a) = b - c; \text{ whence } x = 3b + c - 2a.$$

The second equation then gives—

$$y = 4a - 5b - 2c.$$

Rapid Analysis of Mixtures of Gases.—In gas works and also in many iron and steel works, it often becomes necessary to make a number of analyses of mixtures of gases daily, which, of course, is only possible with simple apparatus. The earliest and simplest form of apparatus was a tube for the estimation of carbonic acid, very much like an inverted burette, used by C. Stammer. This tube was further modified by F. M. Raoult, who used two stopcocks, one above and the other below; and to the upper stopcock was attached a funnel, which serves to introduce the chemicals in solution for treating the gas. After treating the gas, Raoult washed out the chemicals used with water introduced through the funnel, and the gas was measured by bringing the tube to a nearly horizontal position and allowing water to run in through the funnel.

Wilkinson modified this tube of Raoult by placing it in a wider tube having a stopcock below, and omitting the stopcock upon the lower end of the measuring tube. By this means he could adjust the pressure upon the gas by adding water to or drawing it from the exterior tube.

But the difficulty with these methods is the necessity of washing out the chemicals used to absorb the various gases. For example, after

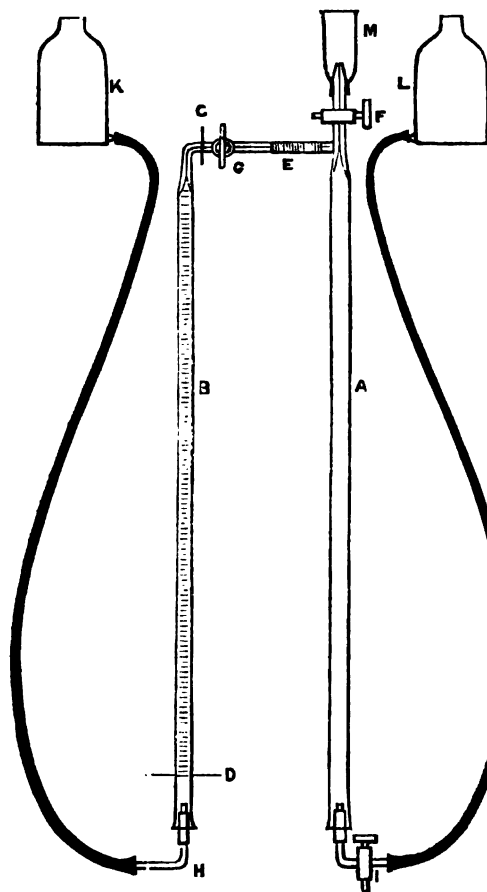
treating a gas mixture with potassium pyrogallate, it is necessary to wash out all the pyrogallate before adding bromine to absorb the illuminants; otherwise the bromine is absorbed by the alkali before it can act upon the gas. To obviate this difficulty and one or two others, Mr. Arthur H. Elliott uses the apparatus shown in fig. 19, next page. The tube A is of about 125 c.c. capacity, whilst B, although of the same length, holds only 100 c.c. from the mark D, or zero, to the mark on the capillary tube at C, and is carefully graduated into $\frac{1}{10}$ c.c. The attachments to these tubes below are seen from the drawing, except that the stopcock I is three-way, with a delivery through its stem. The bottles K and L hold about one pint each. The tubes A and B are connected above with one another and with the funnel M, by capillary tubing about 1 millimetre in internal diameter. There is a stopcock at G and another at F, while the funnel M, holding about 60 c.c., is ground to fit over the end of F above. At E is a piece of rubber tubing uniting the ends of the capillary tubes, which are ground off square to make them fit as close as possible.

In beginning the analysis of a mixture of gases, the stem exit of the three-way cock I is closed by turning it so that L and A are connected through the rubber tubing; the stopcocks F and G are opened, and water is allowed to fill the apparatus from the bottles K and L, which have been previously supplied. When the water rises in the funnel M, and all air-bubbles have been forced out of the tubes, the stopcocks F and G are closed, the funnel M removed, and the tube delivering the gas to be tested attached in its place. By now lowering the bottle L slowly, and simultaneously opening the stopcock F, the tube A is nearly filled with gas, and the stopcock F is closed. The tube delivering the gas is now removed, the funnel M replaced, the bottle L raised, the bottle K lowered, and by opening the stopcock G the gas is transferred to the graduated tube B. By placing the bottle L on a stand at about the level of the water in A, the level in B and in the bottle K can be adjusted to the zero point, and the stopcock G is closed. The excess of gas in A is expelled by opening the stopcock F and raising the bottle L. The gas remaining in the capillary tube between C and the vertical part is disregarded, or in very careful work it may be measured and an allowance made in not filling the tube B quite to the zero mark, but usually it is too small to be worth notice.

Having measured the gas to be tested, it is now transferred by means of the bottles K and L into the tube A, and the fluid chemicals added by placing them in the funnel M and allowing them to flow down the sides of the tube slowly, care being taken *never* to let the fluids run below the level of the top of the vertical tube in the funnel. It is best to have a mark on the outside of the funnel at least $\frac{1}{2}$ of an inch above the top of the level of the vertical tube, and never to draw the fluid down below this point.

Having treated the gas with the reagent, it is transferred by means of the bottles to the tube B, to be measured. If the reagent gets into the horizontal capillary tube, the passage of a little water from the bottle K will remove it, before transferring the gas. When the gas residue is in B, and the fluid in A has been adjusted at the mark c on the horizontal tube, the stopcock G is closed, the bottle K is lowered till the level of water in it and that in the tube B are the

FIG. 19.



same, and the reading is then made. The tube A is now filled with the reagent just used and water. By turning the stem of the three-way cock I, so that it communicates with A, and also opening the stopcock F, the contents of the tube can be run out, and water run through the funnel M to clean the tube for a new absorption. When the tube is clean, by turning the stopcock I, so that A and L communicate, the water is forced into A, and the whole is ready to receive the gas for new treatment. By this means the gas is removed from the action of the water used to wash out the chemicals, and the chemicals are completely removed from any interference with each other when treating a mixture of gases. In using this

apparatus the solutions are added in the following order :

1. *Potassic hydrate*, to absorb carbonic acid (also sulphuretted hydrogen and sulphurous acid if present).
2. *Potassium pyrogallate*, to absorb oxygen.
3. *Bromine*, to absorb illuminants, like olefiant gas and acetylene ; and after the absorption is complete, and the bromine vapours cause

an expansion, a little potassium hydrate is added, to absorb these vapours before the gas is transferred and measured.

4. *Copper Subchloride* in concentrated hydrochloric acid solution, to absorb carbonic oxide. After this absorption is complete the gas is transferred to the measuring tube, the contents of the tube A run out, the tube washed, and filled with water from the bottle L. The gas is now transferred to A, and treated with potassium hydrate solution to absorb hydrochloric acid vapours before the final reading is made in B.

The treatment up to this point takes from 20 to 30 minutes, according to the amount of practice the operator has had with the apparatus. The gas residue still contains marsh gas, hydrogen, and nitrogen. By removing the funnel M, and attaching in its place a rubber tube communicating with an explosion eudiometer in a deep cylinder of water (both eudiometer and rubber tube being drawn full of water), a portion of the gas residue can be mixed with oxygen, exploded, and the contraction and the carbonic acid estimated, the marsh gas and hydrogen being calculated by the usual formula. The nitrogen is found by the difference of the addition of the other constituents and one hundred.

The explosion tube is simply a tube like A without the lower attachment and the lateral capillary tube above, the funnel M being retained; the two platinum wires are fused into the glass near the top to give the spark for ignition. It is only necessary to clamp this tube down upon a piece of cork in a vessel of water during explosion, and adjust the water-level in a tall cylinder of water when making the readings of contraction and absorption of carbonic dioxide.

The whole analysis can be readily completed in 45 minutes, and with due care gives results that are practically correct.

The great advantage of this apparatus over the single tube method is, that the gas is not submitted to the action of the water used to wash out the chemicals, which is found to reduce the volume of the illuminants by 2 per cent.

Of course this method will not compare with the methods of Bunsen and others, where very delicate readings and nice precautions are taken, but it gives very good results for rapid work, and answers every purpose in every-day practice in a gas or metallurgical works.

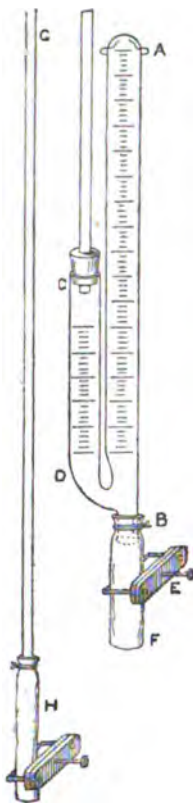
The water used in the apparatus should be of the same temperature as the room in which the analysis is made, and by careful handling little or no chemicals get into the bottle L.

When working in a warm place the tube B should be surrounded with a water-jacket to prevent change of volume in the gas while under treatment.

Thomas M. Morgan has designed an apparatus which is simple in construction, and requires but a small supply of mercury. The eudiometer tube A B (fig. 20) is drawn out at B until it has a diameter of 5 or 6

millimetres ; C D, a shorter piece of the same tubing, is sealed on at one side in the manner shown in the figure, and both tubes have corresponding millimetre scales etched upon them. The capacity of the divisions on A B must be known, and can be estimated by Bunsen's method. The same tube has platinum wires at A, and to B a piece of strong caoutchouc tubing is firmly secured and provided with a clamp, E. The apparatus is filled with mercury through F or C ; in the former case C must be closed with the cork, in the latter B F is compressed by the clamp E.

FIG. 20.



If C D be kept closed with a cork, the gas may be introduced by a small funnel at F, when the apparatus is held obliquely over the mercury trough, with C D undermost ; or a delivery-tube may pass down C, while E is opened sufficiently to allow the displaced mercury to escape ; or should the gas be in a sealed tube, the latter is attached to F, E is opened for the expulsion of enclosed air, and the point is then broken off ; if the gas is under pressure its admission may be regulated by stopping the end C with the thumb.

Before measuring, the mercury in the short limb is brought to a proper level by allowing a sufficient quantity to flow out at B ; and that a known temperature may be quickly arrived at, the apparatus is placed vertically in a cylinder of water, the short limb being fitted with a long tube at both ends, as shown in the figure ; the volume, temperature, and pressure are then read off.

Any absorbent to which the gas may have to be submitted is placed in the short limb and caused to pass into the long one by allowing mercury to run out below until a sufficient quantity has entered ; the short limb is then filled up with mercury, closed, and by agitation the absorbable constituent is removed, or the apparatus may be let stand the requisite time.

The absorbent is removed by means of a stout glass tube, G H, 1 millimetre internal diameter, and considerably longer than the eudiometer ; one end has a strong caoutchouc tube and clamp attached to it ; the other, after being rubbed with a little grease, is inserted at F and tied sufficiently tight to prevent escape of mercury, and yet to allow of freedom of motion up and down. By gradually opening the clamp E, the air is carried out of this tube and it is left filled with mercury. The clamp H is then closed, that at E is opened to its fullest extent, and the tube is thrust up until within 2 millimetres of the absorbent ; then, as a slow stream of mercury is

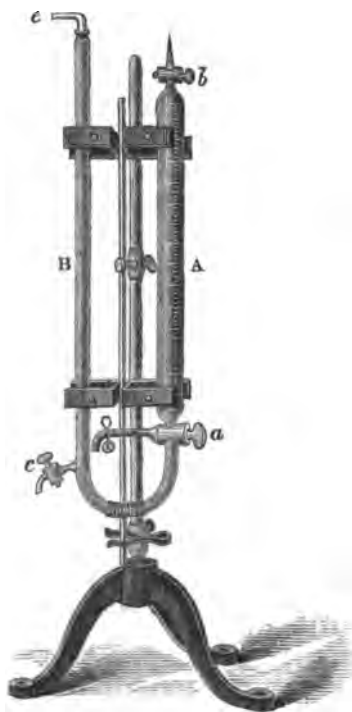
allowed to descend, it is alternately raised into the liquid and pulled down below it. Portions of absorbent and mercury thus follow each other down the tube, but it is evident that if a proper proportion of the latter be not drawn in, the current will cease. After one or two trials it is not difficult to leave a meniscus free from liquid; should any of the gas enter, it may be expelled again by quickly compressing the tube at the bottom. In order to obtain the residual gas saturated with aqueous vapour of normal tension, a little pure water may be introduced and removed in the manner described.

An estimation of nitrates and nitrites by Frankland's method may be made in this apparatus, and it can also be used in an organic analysis by Schulze's method.¹

The apparatus may be strengthened and made more convenient for manipulation by attaching it to a light wooden frame.

Clemens Winkler proposes the following apparatus:—It consists of a two-limbed tube, fig. 21, one limb of which, A, can be closed airtight by two slightly-greased glass taps, *a* and *b*. This shut-off portion of the tube contains about 100 c.c., and it is once for all carefully measured, and the amount inscribed upon the glass. This tube, which we may call the measuring-tube, is graduated from tap to tap into cubic centimetres and decimal parts thereof, the divisions being carried out on the narrower parts of the tube close to the taps. The measuring-tube serves for the reception of the gas in question, and is filled with it by opening both taps, and drawing

FIG. 21.



the gas through by means of an aspirator, until it is certain that all atmospheric air is expelled. The tap communicating with the aspirator is then first closed, and afterwards the one through which the gas enters. If the filling of the tube is not effected by means of an aspirator, but by connection with an apparatus in which the gas is generated, or with a gasometer, or under the pressure of a column of liquid, the outlet-tap of the measuring-tube is likewise closed first, and the entrance-tap last. The extra pressure is then got rid of by

¹ *Watts's Dictionary*, 1st suppl., p. 143.

momentarily opening one of the taps, and the gas is thus brought in equilibrium with the external air. We have also to be satisfied that the gas to be examined is saturated with watery vapour; this is effected by allowing it, before entering the measuring-tube, to pass through wet cotton-wool, which serves also to remove mechanical impurities, such as soot, flue-dust, &c.

When the tube *A* has been filled, with the above-mentioned precautions, the next step is the estimation of the several gaseous constituents by an absorptio-metric process. The limb *B* serves for the reception of the absorbing liquid; it is selected wider or narrower as the case requires, and it is connected with the limb *A* by means of a piece of caoutchouc tubing. On pouring the absorbing liquid into the tube *B*, there is formed under the tap *a*, affixed to the measuring-tube, a collection of air, which must first be removed. For this purpose the tap is provided with two perforations; the one is the ordinary transverse aperture, and serves to place both limbs of the tube in connection; the other goes in the direction of the tap-handle, which terminates in a pointed tube, which again can be closed by means of a piece of caoutchouc tube and a pinch-cock. In this manner it is practicable to let out the included air through the longitudinal aperture of the tap *a*, and, when this has taken place, to prevent the liquid from escaping by means of the pinch-cock. This construction of the tap also enables the measuring-tube to be placed in direct communication with the external air. The different positions which may be given to the tap *a* are seen in fig. 22.

Position *a* connects both limbs of the tube, position *b* connects *B* with the external air, and position *c* places the latter in connection with the measuring-tube *A*. After filling the measuring-tube with the gaseous mixture, the tap *a* is in the position *b*, and a cautious opening of the pinch-cock releases the enclosed air through the liquid in *B*. The gas and the liquid are now only separated by the tap *a*; by turning this round 90° , it takes the position *a*, fig. 22. A communication between both limbs is thus effected, and absorption begins, aided by the pressure of the column of liquid. To expedite it, however, the support bearing the tubes is so arranged that they can be alternately placed either horizontally or vertically. Before being placed in a horizontal position, the tap *a* is placed in the position *b*, fig. 22, and the tube *c*, bent at right angles, is connected with the limb *B*, in order to prevent the escape of the liquid when the tube is inclined. In the horizontal position of the tubes the absorption is very active, as may be perceived if the tube be replaced in the vertical position, and the tap *a* reopened; immediately a fresh quantity of liquid forces its way into the measuring-tube. This alternating inclination of the tubes, the tap *a* being closed each time, is continued until no further entrance of the liquid into the measuring-tube can be perceived—a result which is mostly effected in a few minutes. It is now necessary

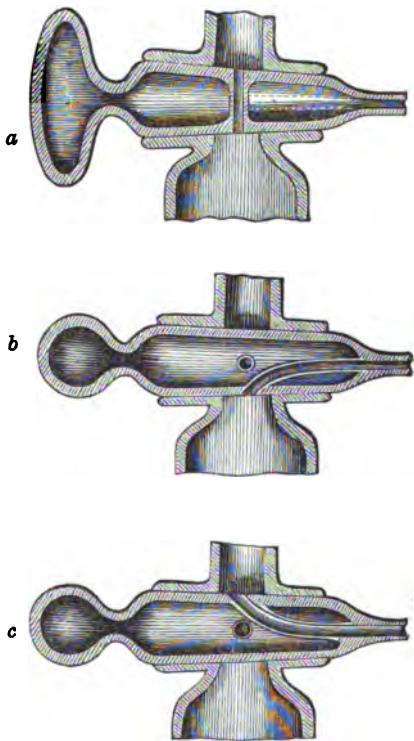
to bring the liquid in the two connected tubes to the same level, which is effected by the exit-tap *c*, fig. 22. The volume of liquid which has entered into *A* represents the number of c.c. of absorbed gas, and when it is multiplied by 100, and divided by the total capacity of the measuring-tube, the percentage of the absorbed constituent is found.

From the above it appears that only one gaseous constituent, or the sum of several, can be estimated at once. If a complete analysis is required, as many apparatus can be used at once as there are gaseous constituents to be estimated. The measuring-tubes are connected together with caoutchouc tubes and filled at once.

The analyst has thus the advantage of operating upon a set of portions filled under the same conditions of temperature and atmospheric pressure, and equally saturated with watery vapour, so that the customary corrections for temperature may be dispensed with. The estimations take so little time that an alteration of the volume of the gas from a change of temperature is not to be feared. Care must be taken that the various absorption liquids have all the same temperature. To regulate the temperature of the gaseous mixture, it is allowed to pass through a bottle of mercury, which is kept along with the absorbents. If it is required to estimate relatively small amounts of a gaseous constituent, a somewhat modified construction of the measuring-tube is needful. The lower part nearest to the tap *a* is made narrower, so as to admit of a more accurate graduation, say to $\frac{1}{10}$ of a c.c. In this case the graduation need not be continued for the whole length of the tube.

1. Aqueous Vapour.—All gases are saturated with aqueous vapour prior to measurement. The estimation of the water present is not necessary in every case. If it is required to find the amount of aqueous vapour in a gaseous mixture, concentrated sulphuric acid is used as

FIG. 22.



absorbent liquid. By inclining the tubes a few times, the gas is dried completely. Before reading off, the sulphuric acid is allowed to stand for a few minutes.

If the gas under examination contains originally a certain amount of water, without being saturated, two estimations are required.

One apparatus is filled direct with the gaseous mixture, without allowing it to pass through the tube filled with wet cotton-wool; whilst another is filled with gas which has been thus saturated. The difference which appears between the two subsequent measurements with sulphuric acid corresponds to the volume of aqueous vapour which the gas took up in passing through the damp cotton wool.

108·7 c.c. air, treated direct with sulphuric acid, required 0·9 c.c. = 0·82 volume-percentage of water.

106·8 c.c. air, saturated with aqueous vapour, required 2·3 c.c. sulphuric acid = 2·11 volume-percentages of water.

The water taken up for saturation amounted, therefore, to 2·11 - 0·82 = 1·29 volume-percentages.

The estimation of oxygen in the air saturated with aqueous vapour yielded 20·44 per cent.; consequently, the original unsaturated gas—

$$100 - 2·11 : 100 - 0·82 = 20·44 : x ;$$

$$x = 20·7 \text{ per cent. (measure) oxygen.}$$

Hence it follows that the air in question contained—

Oxygen	20·70
Nitrogen	78·48
Aqueous vapour	0·82

2. Carbonic Acid.—The estimation of carbonic acid is not only very rapid, but yields results which, in point of accuracy, leave nothing to be desired. A moderately concentrated solution of the potassium hydrate is used as absorbent.

3. Nitrogen.—The direct estimation of nitrogen has not hitherto been found possible. It is estimated from the difference, and, as a matter of course, the residue, representing nitrogen, is burdened with every error in the whole analysis.

4. Sulphurous Acid.—The method employed for carbonic acid can be used in many cases where it is needful to ascertain the amount of sulphurous acid present in a gaseous mixture. The absence of carbonic acid and of other gases soluble in alkaline solutions must, of course, be ascertained with certainty; otherwise the result would be found too high. For certain furnace gases produced without the use of fuel, *e.g.* by roasting pyrites in kilns, the potash process is directly applicable, since the error occasioned by the trace of carbonic acid present in the air supporting the combustion is too trifling to be appreciated.

If, in a gaseous mixture under examination, the other gases absorbable by potash-lye are present in addition to sulphurous acid, a solution

of iodine in potassium iodide is used as absorbent, of the strength of the deci-normal solution used in volumetric analysis. It must be remembered that this liquid is also not quite without action upon carbonic acid, which it dissolves mechanically to some extent, as water does. This difficulty is got over by using a solution through which a current of carbonic acid has been passed for some hours. When the iodine solution penetrates into the measuring-tube, it is immediately decolourised, and it is only after repeated inclinations that an excess of iodine becomes perceptible within the tube. This excess must be present if the estimation is to be correct. If the liquid remains colourless, it is a sign that the solution of iodine employed is not sufficiently concentrated, and that in consequence a part of the sulphurous acid is not oxidised, but mechanically dissolved.

The volumetric estimation of oxygen in gaseous mixtures is effected by means of a solution of pyrogallic acid in potash-lye. The liquid is prepared specially for each estimation by dissolving 1 to 2 grammes of pyrogallic acid in a little water, and adding about 100 c.c. of a tolerably concentrated potash-lye. The absorption is rapid at first, but becomes slow towards the end. Hence it is prudent, after the action is apparently over, to leave the liquid still for some minutes in contact with the gas, turning the tubes occasionally. Before reading off it is necessary to wait till the brown froth has subsided. An estimation requires about 10 minutes.

If, in a mixture containing oxygen, gases are present which are absorbable by alkaline liquids, such gases are naturally absorbed by the potassium pyrogallate. This is, e.g., the case if carbonic acid is present. Under such circumstances, the carbonic acid present is estimated separately in one apparatus by absorption with potash-lye, and in a second the joint amount of oxygen and carbonic acid is absorbed by potassium pyrogallate, and the net volume of oxygen is then found by subtraction. If, in addition to oxygen, nitrogen, and carbonic acid, sulphurous acid be also present, we estimate:—

By potassium pyrogallate, $O + CO_2 + SO_2$

By potash-lye, $CO_2 + SO_2$

By iodine solution SO_2

The residue is nitrogen.

5. Nitric Oxide and Nitrous Acid.—The volumetric estimation of the lower nitrogen oxides is a matter of great importance. A saturated solution of green vitriol seems to have a sufficient absorptive power for the volumetric estimation of nitric oxide, though the numbers obtained are not, so far, as constant as might be desired. The absorption of nitrous acid can be effected by means of concentrated sulphuric acid. Whilst, however, we may assume with tolerable certainty that nitrous acid may be absorbed by means of sulphuric acid in gaseous mixtures containing nitric oxide, it is questionable

whether, conversely, nitric oxide can be estimated by green vitriol in presence of nitrous acid. It appears that green vitriol absorbs nitrous acid also in not inconsiderable amount, whether by simple solution or by some chemical change being not yet decided. If this is confirmed, then in all cases where the two gases are jointly present, it will be requisite to estimate the nitrous acid direct in one apparatus by sulphuric acid, whilst the nitrous acid must be withdrawn from the gaseous mixture as a preliminary to the estimation of the nitric oxide by green vitriol in a second apparatus. This would be effected by passing the mixed gases through a washing-bottle filled with sulphuric acid, previous to their admission into the measuring-tube.

6. **Chlorine.**—The estimation of chlorine can be effected in most cases by means of a moderately-concentrated solution of the potassium hydrate. The process is rapid, and can be recommended when no other gas capable of absorption by alkalis is present along with the chlorine. An admixture of such gases, especially of carbonic acid, is found when chlorine gas is evolved from a calciferous manganese. In such cases the chlorine must be absorbed by a liquid which has no action upon carbonic acid. A solution of iron protochloride, mixed with hydrochloric acid, answers the purpose satisfactorily; it must, however, be previously saturated with carbonic acid, by passing that gas slowly through it for some hours.

7. **Hydrochloric Acid.**—Potash-lye is employed with satisfactory results. If carbonic acid is simultaneously present, hydrochloric acid gas might possibly be absorbed by water previously saturated with carbonic acid.

8. **Ammonia.**—The absorption of ammonia is most readily effected by means of dilute sulphuric acid.

9. **Sulphuretted Hydrogen.**—A solution of potassium hydrate absorbs this gas rapidly and completely. If carbonic acid is simultaneously present, the case is not free from difficulties. Pass the gaseous mixture through a washing-bottle filled with a concentrated solution of iodine previously saturated with carbonic acid; in this the sulphuretted hydrogen is oxidised and the sulphur deposited. The remaining gases, including the carbonic acid, pass on into the measuring-tube. The carbonic acid is then estimated in one apparatus, in the portion of gas thus freed from sulphuretted hydrogen, by means of potash-lye. A second apparatus is filled with the gas in its original condition, and carbonic acid *plus* sulphuretted hydrogen. It may here be remarked that sulphuretted hydrogen is advantageously collected over petroleum, by which it is not at all absorbed.

10. **Carbonic Oxide.**—The discovery of a simple and accurate method of estimating carbonic oxide in a gaseous mixture is of the utmost importance for the right management of combustion under a variety of circumstances. The absorbent used is a solution of copper subchloride in hydrochloric acid. The subchloride for this purpose

was obtained by precipitating cupric chloride with stannous chloride. The white crystalline precipitate is first repeatedly washed with cold water by decantation, then twice washed with strong alcohol, and finally once with ether. It is then dried at 80° to 90° C. in a current of carbonic acid. The white salt is preserved in airtight bottles. It is easily and plentifully dissolved in hydrochloric acid, and if a spiral of copper wire is kept in the liquid, reaching from the bottom to the neck of the bottle, and if the latter is kept carefully stoppered, it may be preserved for a long time free from change. The solution should not be too concentrated.

A solution suitable for the purpose is obtained by saturating hydrochloric acid at sp. gr. 1.11 with copper subchloride. The liquid absorbs the gas very greedily.

The estimation of carbonic oxide in gaseous mixtures whose other constituents act neither chemically nor mechanically upon the copper subchloride offers no difficulties. Less easy is the estimation when other absorbable gases are present. The error which might arise from the presence of carbonic acid may be evaded by saturating the solution of copper subchloride previously with carbonic acid. Oxygen has a very disturbing influence, and must be removed before the estimation of the carbonic acid. This is effected by allowing the gaseous mixture, before its entrance into the measuring-tube, to pass through a Liebig's potash apparatus filled with the solution of pyrogallic acid in potash-lye. In this manner oxygen, carbonic acid, &c., are absorbed, and only carbonic oxide, hydrogen, and nitrogen passed on into the measuring-tube. The amount of carbonic oxide is then estimated in the gas so treated, while the oxygen, carbonic acid, &c., are estimated in separate portions of the original gas.

Estimation of Nitrous Oxide.

A. Wagner examined whether nitrous oxide could be estimated by means of its oxidising action upon an ignited mixture of chromium sesquioxide and sodium carbonate in the absence of air, and was completely successful. The nitrous oxide decomposed can be estimated either by the volume of the nitrogen liberated or by the quantity of sodium chromate formed, since 1 volume nitrous oxide yields 1 volume nitrogen, and 1 part chromium oxide requires 0.8186 oxygen for conversion into chromic acid. The author found by especial experiments that by heat alone, in the absence of the mixture of sodium carbonate and chromium sesquioxide, only 28.2 per cent. of the nitrous oxide is decomposed. A mixture of equal volumes nitrous and nitric oxide is entirely decomposed under the same conditions, giving up all its oxygen, whilst any excess of nitric oxide escapes unchanged.

Sensitive Reagent for Gaseous Ammonia.

Gustav Kroupa dissolves magenta in water, and adds dilute sulphuric acid until the yellowish colour passes into a yellowish-brown.

Unsize paper is saturated with this solution, and then appears yellow, but if exposed to the vapour of ammonia it takes a crimson colour. The paper must be preserved in stoppered bottles.

Standard Soda Solution.

Gerresheim has published an article on ammoniacal mercury compounds, wherein he calls attention to the pronounced basic properties of the so-called Millon's base, which is obtained by the action of ammonia upon mercuric oxide. He states that a soda solution to which hydrochloric and sulphuric acid, &c., have been added can be freed from these by shaking with Millon's base. Mercury is not found in the solution. This method has been employed in order to obtain a chemically pure standard soda solution from the ordinary so-called pure caustic soda, and we have found all that the author claims verified. The soda contained large quantities of chlorine, sulphuric acid, and also silicic acid, and carbonic acid. For 2 litres soda solution about 80 grammes of Millon's base are employed. The chlorine disappears first, then carbonic acid, silicic acid, and sulphuric acid. The process is complete after about one week's standing, the mixture being shaken about once or twice each day.

Allow the Millon's base to settle in the solution, and draw off with a syphon as required. Shaking from time to time removes any carbonic acid which in the course of time may be absorbed by the soda. Millon's base absorbs carbonic acid from the air rapidly, and is also not easily filtered and washed. It is therefore not completely washed free from the last traces of ammonia, as it is preferable to remove these by the addition of a small quantity of mercuric oxide when the Millon's base is brought into the soda solution.

New Alkalimetric Indicator.

Professor Lunge and Dr. Greville Williams recommend the colour 'Orange III.' of Poirrier as a substitute for litmus. It is sensitive to 1 part of sulphuric acid in 100,000 parts of water.

Dr. Williams says:—The solution of the indicator which I employ is made by dissolving 1 centigramme in 100 c.c. of distilled water, and contains therefore 1 part in 10,000. Even at this great dilution the liquid is of a full orange colour. It is worthy of remark that 1 centigramme of the substance is sufficient for 500 estimations of acid or alkali; its cost is consequently inappreciable. It has also the advantage over litmus that its solution is less liable to decomposition on keeping.

The quantity of the solution of the indicator, of the strength given above, to be used in each estimation is from .1 to .2 of a cubic centimetre. When this small quantity is added to a solution containing an alkali to be tested, there is no perceptible colouration as long as it is alkaline; but the faintest trace of acid turns the solution a pale

but distinct pink tint, which is easily seen if the beaker be placed upon a sheet of white paper.

The best way of applying the test is, after each addition of acid from the burette, to allow a drop of the indicator to fall on the surface of the liquid in the beaker after the contents have been well stirred. By this mode of proceeding the indicator is distributed over a smaller space, and the reaction is therefore more distinct.

An immense advantage which this indicator possesses over litmus is that it is entirely unaffected by carbonic acid; the solution need not therefore be boiled, and the operation consequently takes much less time; in fact, four operations can be made in the same time as one with litmus.

The colour in question is also known as Helianthine, and as Tropæoline D., or as Professor Lunge suggests, 'Methyl Orange.'

Mr. P. Casamajor has been led to adopt an entirely new form of burette, which is represented in figs. 23 and 24. It consists of a cylindrical tube closed at the bottom, and inserted in a stand or foot made of japanned tin. The cylindrical portion of this tin stand is only partially soldered on the flat part, to allow the portion left free to act as a spring in holding the glass cylinder tightly.

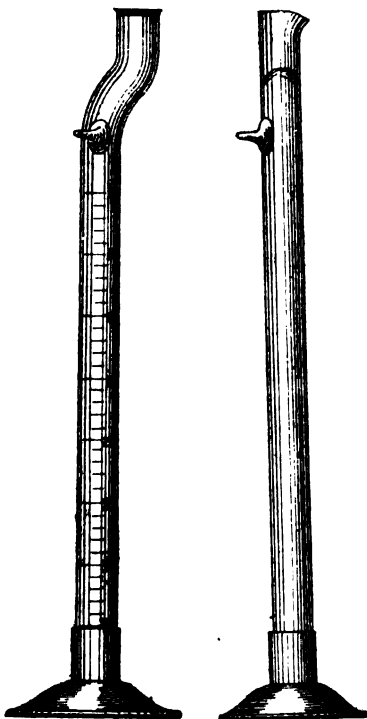
The upper portion of the glass tube has the shape shown in fig. 23, to prevent the liquid from running out when the tube is inclined.

Immediately under the curved portion of the burette is a beak, from which the liquid drops when the instrument is inclined and properly turned. By making a transverse section through this beak we obtain figs. 25 and 26, which show the shape of the beak, and its position in relation to the stem for two positions of the tube.

To allow the liquid to drop from the burette it is inclined as in fig. 25, in which position the curved portion at the upper end prevents the liquid from pouring out. Keeping the tube inclined as in this figure, we may either prevent the outflow of its contents or allow it to run with more or less rapidity. To effect this it is merely necessary

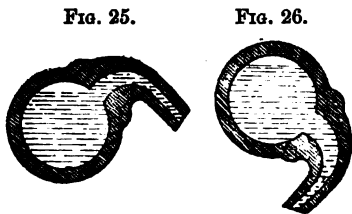
FIG. 23.

FIG. 24.



to turn the instrument around its own axis, so that the beak may be either raised or lowered, as shown in figs. 25 and 26. When the beak is allowed to take the position shown in fig. 25, the liquid in the tube does not run out, while in the position shown in fig. 26 the drops run out quite rapidly. At some intermediate point it will be found that the liquid runs out slowly in drops, which may be accelerated or retarded by turning the tube round its axis, but without changing the inclination of this axis.

The motion imparted to the burette by holding it in the hand and simply turning it round its axis is an easy one for the operator, who is not obliged to watch the liquid in the instrument with any degree of attention. As the liquid runs out of the burette it becomes necessary to incline its axis more and more, to keep a supply of liquid near the beak; but there is no difficulty connected with this, as the liquid runs out with equal ease when the instrument is full to the 0 mark as when it is nearly empty. When the changes which occur in the liquid under examination indicate that the operation is nearly ended, the liquid may very easily be made to fall in single drops by turning the beak down gradually, and raising it again with a sudden motion. This is easily learnt by a little practice, and does not require a close watch on the contents of the burette.



The most convenient position for the operator is to hold the tube almost horizontally and to let the foot roll on a block of proper height, while the necessary motions are given to the instrument by holding it with one hand near its open end. This presents the additional advantage that the portion which becomes heated by the hand is not in contact with the liquid contents of the tube.

Whenever it becomes necessary to lift the instrument, the beak should be previously raised by turning the tube, as otherwise a drop of liquid may escape and run down the side of the tube. After the operation is ended, the burette should be left in a vertical position for some minutes, to allow the liquid to run down before reading the indication of the scale. As the beak holds by capillarity a certain quantity of test liquor, it will be found convenient to keep it full whenever the indications of the scale are observed. This beak usually becomes filled of itself at the time of filling the instrument with test liquor. The open end of the burette may be provided with a lip on the side opposite to the beak, as shown in fig. 24. This is to allow the test liquor to run out faster when desired. Many chemists are unwilling to trust to volumetric analysis, for fear of the changes of volume which are due to changes of temperature. They are, however, willing

to use the solutions of this method of analysis, and they have adopted a gravimetric system, which consists of weighing instead of measuring their test liquors. For this manner of using test solutions the gravimetric burette represented in fig. 28 may be used. The manner of using this burette is precisely the same as for the volumetric instrument, and it does not require any further explanation.

The weight of test solution used in an analysis is best determined by double weighing. The flask or gravimetric burette, containing a greater quantity of test solution than will be required by the analysis, is placed on the scales and counterbalanced with shot or any other material. After the operation is ended, the flask should be replaced on the same pan of the scale and be made to counterbalance the original quantity of shot by adding weights, which represent the weight of test solution that has been used. A common balance weighing 200 grammes and turning to 1 centigramme is sufficient for this method of testing.

FIG. 27.



FIG. 28.



Estimation of Free Oxygen in Water.

Mr. C. C. Hutchinson gives the following account of a modification of Schützenberger's process. The reducing agent is sodium hydrosulphite prepared as follows:—A concentrated solution of caustic soda, sp. gr. 1·4 was taken; sulphurous anhydride was passed through it till the liquid was thoroughly saturated and smelt strongly of the gas. The yellow liquid (which was kept cool during the process of saturation by immersion in cold water) is sodium bisulphite; it increased slightly in bulk, and was reduced to the sp. gr. of about 1·34. 100 grammes (75 c.c.) of this solution were then briskly agitated in a flask with 6 grammes of powdered zinc, air being excluded; an elevation of temperature occurred, the bisulphite being converted partly into the hydrosulphite, together with the formation of sodium sulphite, and zinc sulphite. After agitation for about five minutes, the liquid was allowed to cool; 400 c.c. of water recently boiled were added; 35 c.c. of milk of lime, containing 200 grammes of calcium oxide per litre, were also added, and the mixture allowed to stand until clear, when it was decanted off into well-stoppered bottles and

kept in the dark. The lime solution not only precipitates the zinc salt, but also renders the solution less absorbent of free oxygen, although it acts very rapidly upon dissolved oxygen. Before use this was further diluted with three times its bulk of distilled water recently boiled.

The liquid recommended by which the change of colour detects the completion of the process is either sodium sulphindigotate, or Coupier's aniline blue; 10 grammes of the extract of indigo are recommended to be dissolved in one litre of water, the product being kept in well-stoppered bottles, also in the dark.

An ammoniacal solution of pure copper sulphate is also recommended to be made, containing 4.46 grammes (or more correctly, 4.471 grammes) of the crystallised salt per litre. This is to be used for the standardisation of the above two solutions.

Since the reducing agent is so sensitive to the presence of oxygen, it is necessary to make the estimations in an atmosphere of pure hydrogen. To insure the purity of the hydrogen, it is passed through a solution of silver nitrate, in addition to the sulphuric acid and the tube containing pieces of caustic potash.

We begin by finding the volume relation between the indigo and hydrosulphite. The burettes of the apparatus are filled, one with indigo carmine solution, the other with hydrosulphite; a rapid current of hydrogen is passed through the apparatus, a small quantity of warm distilled water added, and this coloured by the addition of a small quantity of indigo. We now add cautiously the hydrosulphite; the blue solution turns first green, and finally to a clear yellow tint. If the whole of the air has been expelled from the apparatus, the yellow tint will remain unchanged; the slightest trace of oxygen causes the surface of the liquid to become blue. A known volume of indigo (25 c.c.) is now added, and the hydrosulphite solution again run in until the yellow tint appears, indicative of the reduction of the whole of the indigo. The colour change is exceedingly sharp, one drop being sufficient to change the colour from green to yellow. If the solution be acid, the blue colour changes first to red, and finally the yellow tint appears.

We next require to find the reducing power of the hydrosulphite in terms of oxygen, finding from this the amount of oxygen any volume of the indigo will yield. This being a stable solution, the hydrosulphite (being liable to change) can be readily standardised at any future time. This reducing power can be found by finding the quantity necessary to reduce the ammonia copper solution, i.e. the amount which brings the blue solution to a colourless state, by the reduction of the cupric to cuprous oxide; 10 c.c. of this solution yield 1 c.c. of oxygen (0° C. 760 millimetres pressure) to the reducer. 25 c.c. are operated on in a smaller apparatus similar to the one used for the water estimations. It was found, however, that the colour change in this

plan is so indefinite and difficult, even to the practised eye, to detect, that the exact point cannot be determined with any degree of certainty

The method for the estimation of oxygen contained in a water is as follows. Owing to the change which the hydrosulphite undergoes, it is necessary that a comparison between it and the indigo should be made each day. After this has been done and the apparatus freed from air by means of the hydrogen, 200 c.c. of warm water (temperature about 50° C.) are then added; 50 c.c. of indigo are now run in. This is usually effected in portions of about 15 c.c. at a time, decolourising each portion by means of the hydrosulphite, thus utilising this step for the comparison of the two reagents; effecting thereby a saving of time and material. The liquid in the apparatus being now brought to the yellow neutral tint, a measured volume of the water under experiment is added—75 c.c. is a convenient quantity—taking care that no air is admitted at the same time. The bleached indigo will now become re-oxidised, turning from yellow to blue, in proportion to the amount of oxygen present in the water. The hydrosulphite is now cautiously added until we again arrive at the yellow tint, free from green; a single drop of the reagent is sufficient to effect the colour change at the proper point. From the quantity used we find the amount of oxygen present in the 75 c.c. of water. The operation can be repeated over again on another volume of the water until the apparatus becomes inconveniently full. The temperature of the apparatus must be kept at about 50° C. by the addition of warm water at intervals; the amount of hydrosulphite required becomes gradually less as the apparatus cools, giving the results too low.

Simple Method of Estimating the Temporary Hardness of Water.

V. Wartha, in order to ascertain the alkalinity of spring waters on the spot, with samples not exceeding 10 c.c., and with a single reagent, makes use of a tube of 80 to 40 centimetres long, closed at the bottom, and with a mark showing the capacity of 10 c.c. From this mark upwards the tube is graduated into 0.1 c.c. To estimate the temporary hardness the tube is filled to the lowest mark with the water in question, and a little piece of filter-paper, which has been previously steeped in extract of logwood and dried, is thrown in, thus giving the water a violet colour. Centinormal hydrochloric acid is then added from a dropping bottle till the colour of the liquid inclines to orange. The tube is then closed with the thumb and well shaken. The greater part of the carbonic acid escapes, and the liquid becomes red again. Acid is again added, and the shaking repeated until the next drop of the acid turns the liquid to a pure lemon-yellow, a point which with a little practice is easily reached. The amount of acid used is read off on the tube itself. The author proposes to express the

alkalinity of a water by the number of centimetres of centinormal acid needed to neutralise 10 c.c. He thinks that this method will be found useful both for sanitary and geological purposes.

New Test for Reducing Agents.

Mr. Edwin Smith has published a method of illustrating the de-oxidising property of sulphurous acid, by exposing a slip of bibulous paper, dipped in a mixed solution of iron sesquisulphate and potassium ferricyanide, to the vapour rising from a bit of sulphur burning in air. The iron persalt being reduced to a protosalt by giving up an equivalent of oxygen to the sulphurous acid, a blue reaction takes place with the potassium ferricyanide present in the solution. A solution of sulphurous acid, or of a sulphite or thiosulphate, gives the same result; while only a very slight greenish tinge is imparted to the mixture by a sulphate, except in the case of iron protosulphate. With this exception, a useful test seems to be afforded between sulphites and sulphates. The same test will discriminate a nitrite from a nitrate.

To the mixed solution of iron sesquisulphate and potassium ferricyanide add a few drops of nitric acid; then add a little of the solution to be tested. If the latter contains a nitrite, a greenish-blue precipitate will begin to fall, and quickly increase; if a nitrate, only a slight greenish tinge will be imparted to the test. Nitric oxide or nitric trioxide passed into the mixed solution throws down the same characteristic precipitate which is produced by the decomposition of a nitrite in the previous case. Carbonic oxide will act in the same way, and if a slip of paper dipped in the test-mixture be held over the clear part of a bright coal fire, it turns blue with the carbonic oxide or sulphurous acid there given off. Again, if a bit of phosphorus is dropped into a little of the test-mixture in a porcelain dish, the phosphorus immediately becomes coloured a greenish blue, and on stirring about, gradually imparts the same tinge to the solution. Phosphorous acid may be discriminated from phosphoric acid, just as sulphurous acid is distinguished from sulphuric acid by the blue reaction. Phosphites are also distinguished from phosphates. A solution of phosphorous acid shows the reaction readily on being shaken up with the test-mixture. Lastly, if copper turnings are boiled in the mixed solution for a few minutes, a greenish-blue tint is imparted to it, which becomes gradually deeper with the oxidation of the copper and the consequent reduction of the iron persalt to the state of a protosalt.

Improved Methods of Oxidation.

Professor Storer points out the superior oxidising power of a mixture of ordinary nitric acid and potassium chlorate over that of the mixtures of potassium chlorate and hydrochloric or sulphuric acid commonly used in analysis.

Blowpipe Analysis. Employment of Silver Chloride.

Amongst the phenomena which characterise different bodies before the blowpipe, and serve for their distinction, the colour of the flame is of no small importance, especially when the eye observations are supplemented by the use of a spectroscope. This power of colouring the blowpipe flame, is not, however, exhibited by all bodies with sufficient intensity to enable them to be distinguished by it with certainty, and certain substances, such as hydrochloric acid, are consequently usually employed, with barium, strontium, and calcium compounds, partly to form and partly to set free volatile compounds. By this means, however, although the intensity of the colouration is heightened, its duration is not increased, as the acid evaporates, for the most part, before it has acted sufficiently, so that the colouration lasts only for a few moments. Dr. H. Gericke overcomes this difficulty by the employment, instead of the volatile hydrochloric acid, of a chloride which will retain the chlorine at a high temperature, so that it may only be set free by degrees in small quantities, whilst the body forming its base may be without action upon the colouring power of the body under investigation. For this purpose silver chloride appears to be the best, especially as it may readily be prepared in a state of purity. The best plan is to stir it with water into a thick paste, and keep it in a bottle.

In regard to the action of silver chloride upon the colouration of the blowpipe flame, the author has investigated several compounds of potassium, sodium, lithium, calcium, barium, strontium, copper, molybdenum, arsenic, antimony, and lead, and mixtures of these substances. Silver chloride has no action upon borates and phosphates.

Platinum wire does not answer well as a support, as it is soon alloyed by the metallic silver which separates, and is thus rendered useless. Silver wire is too readily fusible, and also is difficult to obtain free from copper, which may give rise to errors when in contact with the silver chloride. Iron wire is best fitted for experiments with silver chloride, as, from its cheapness, a new piece may be employed for each experiment, whilst the silver may be readily obtained in the form of chloride from the broken pieces.

The results obtained by the employment of silver chloride in comparison with those obtained without this reagent are as follows :—

With potassium compounds, such as saltpetre, potash, &c., the flame is decidedly of a darker colour with silver chloride; and even with potassium ferrocyanide, which, when treated by itself with the blowpipe, colours the flame blue, the addition of silver chloride produces a distinct potassium colouration.

The action of silver chloride upon sodium salts is not so marked, although with some, such as sodium nitrate, common soda, and labradorite, the flame acquires a more intense yellow colour by the addition

of silver chloride. This reagent produces no observable difference with other sodium compounds, such as sodium sulphate and analcime. This also applies to the lithium compounds, some of which give a finer purple-red colour on the addition of silver chloride, whilst upon others it has no such effect.

With calcium compounds silver chloride acts favourably upon the colouring power. Thus, the addition of silver chloride to calcareous spar or gypsum (in the reduction-flame) gives the flame a more distinct yellowish-red colour; but stilbite gives no calcium colouration either with or without silver chloride. With fluor-spar the colouration cannot well be observed, as this decrepitates too violently under the blowpipe.

The action of silver chloride upon barium and strontium compounds is decidedly advantageous, as both the intensity of the colouration and its duration leave nothing to be desired. Sicilian coelestine, which when heated by itself in the forceps scarcely colours the flame, immediately produces a permanent red colouration when heated with silver chloride.

Although it appears from the preceding statements that the employment of silver chloride presents no advantage with some substances, it may be used with good results in the treatment of mixtures of alkalis and earths. Thus, with petalite alone, the lithium colouration is first produced; a slight sodium colouration is afterwards obtained; whilst, with silver chloride, the sodium colouration appears very distinctly after that of lithium. With lithion-mica alone a very distinct lithium colouration is presented, but in the presence of silver chloride, a colour is first produced, which may lead to the conclusion that potassium is present but the lithium colouration is weakened. Rhyacolite, heated by itself in the blowpipe flame, only gives a distinct sodium colouration; but with silver chloride, a slight potassium colouration is first produced, and the colouration of sodium then appears very distinctly; the calcium contained in it cannot, however, be detected by the colouration of the flame, although evident in the spectroscope.

Silver chloride may be employed with still greater advantage with the following metals, but in these cases it is particularly necessary that the operator should become familiar with the colour as well as the spectrum produced by each individual substance.

With copper compounds, such as red copper ore, malachite, copper pyrites, copper sulphate, &c., when contained in other minerals so as to be unrecognisable by the eye, the employment of silver chloride may be of great service, as the smallest quantities of copper, when treated with silver chloride under the blowpipe, give a continuous and beautiful blue colour to the flame. With silver chloride, the presence of copper may be distinctly ascertained by the blowpipe, even in a solution which is no longer coloured blue by the addition of ammonia.

The employment of silver chloride will be equally advantageous with molybdenum, as in this case also the flame gains greatly in intensity. Arsenic, lead, and antimony are already sufficiently characterised, the former by its odour, the two latter by their fumes; but even with these metals silver chloride may be employed with advantage to render their reactions still more distinct. It is only necessary to observe that the greenish-blue flame of antimony appears greener and more like that of molybdenum under the influence of silver chloride.

Silver chloride may also be employed with compounds containing several of the above-mentioned metals. If bournonite be heated in the oxidation-flame of the blowpipe, a fine blue flame is first produced, which indicates lead with certainty; if silver chloride be now applied, copper is also readily shown. The antimony contained in bournonite cannot be ascertained by the colouration of the flame; but this may be easily detected upon charcoal or in a glass tube open at both ends. Native lead molybdate without silver chloride only gives a blue colour to the blowpipe flame; with silver chloride this blue colouration of lead comes out more distinctly, but at the same time the tip of the flame, particularly when the reduction flame is employed, appears of a beautiful yellowish-green colour from molybdenum. With mixtures of arsenic and copper, or antimony and copper, the flame first appears a greyish-blue or greenish-blue colour, from the oxidation of the arsenic or antimony; the copper may be then very easily detected by silver chloride. This applies also to mixtures of arsenic and molybdenum, or antimony and molybdenum; with silver chloride the yellowish-green flame of molybdenum appears distinctly. It will be more difficult to analyse mixtures of arsenic and lead, or antimony and lead, in this manner, and if a compound contains both arsenic and antimony, these two bodies are not to be distinguished with silver chloride under the blowpipe.

Silver chloride is particularly to be recommended in testing metallic alloys for copper. Thus to test silver for copper, silver chloride may be applied to the ends of silver wires, and on the application of heat the smallest quantity of copper will furnish a distinct reaction. This is as sensitive as any of the known copper reactions, and may be performed quickly and easily. In testing metallic alloys for traces of copper, it may be advisable to submit those which contain antimony, zinc, lead, and other volatile metals, to roasting, so as to drive off these metals before the addition of the silver chloride.

Quantitative Spectral Analysis.

M. Hufner illuminates the two halves of the slit of the spectroscope by two pencils of rays, one of which traverses the absorbent, whilst the other can be darkened at pleasure. As a source of light a petroleum lamp is employed, placed in the focus of a lens; half of the

pencil of rays falls at the angle of polarisation upon a mirror, which throws it back upon a parallel mirror not tinned, placed before the upper portion of the slit; a Nicol's prism fixed before the eyepiece serves to decrease the polarised pencil without acting upon the other. Before the lower part of the slit is fixed a double prism formed of a prism of transparent glass and one of smoked glass. It is rendered equal with the Nicol's prism, and the absorption corresponding with a given rotation is deduced once for all. This instrument gives very precise chemical indications.

M. Vierordt in 1871 proposed to divide in two the slit of the spectroscope; the plates of the one portion of the slit being set in motion by micrometer screws, which rendered it possible to equalise the spectrum of a light viewed directly through the narrow portion, and the spectrum of the light after its passage through an absorbent transmitted by the other portion. The intensity of the light within the limits of experiment is proportional to the width of the slit. At present he substitutes for this arrangement two others; in one the four plates of the slit are separately movable, in the other two of the plates are regulated by a screw, and move in opposite directions; the two others are separately movable. The errors of measurement are very trifling.

A New Method of Quantitative Chemical Analysis.

In comparing together the results of a large number of chemical analyses it is seen that the numbers obtained vary between 99.17 to 100.67, giving a difference of about 1.5 per cent., or, supposing a quantity of 1.5 gramme of substance has been taken and the weighings carried to 0.0001 gramme, a difference of 225 units. The analyses here alluded to are by no means those which would be called bad or indifferent, but are such as have been made and published by eminent chemists. It ought further to be remembered that very many analyses yield results varying from 97 to 102 per cent. instead of 100, whilst the really bad ones never see the light at all. Under ordinary circumstances slight differences do not usually affect the result of an analysis, but if it is desired to employ the sum of the substances found to control the results, an incorrect total fails to serve this purpose, as there is no means of knowing upon which of the substances the error really falls. Moreover, in many instances, only small quantities of material are available. A more accurate and improved method of analysis would admit of the employment of smaller quantities, as well as effect a great saving of time and labour.

It would appear that neither the methods and processes in use nor the impurities of reagents are greatly at fault, because it is found that when the same substance is analysed under exactly the same conditions the results often differ. It would therefore appear that accuracy depends chiefly upon the manipulations, among the most

dangerous of which may be mentioned decantation, the removal of substances from a filter, the ignition of the filter-paper, and the calculation of the ash; the employment of a great number of vessels may either add something to solutions or withdraw something therefrom.

Dr. H. Carmichael has proposed a very ingenious apparatus for overcoming these difficulties. His apparatus is represented in the accompanying cuts.

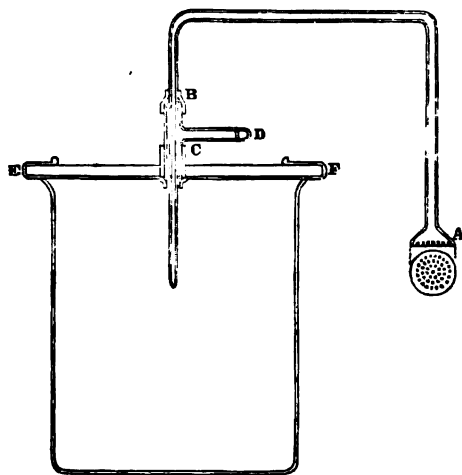
Fig. 29 (represented one-fourth of its natural size) consists of a doubly-bent glass tube, with a funnel-shaped widening at one of its ends, the wider part being perforated with a large number of small holes; the other bend of the glass tube is fitted in the T-shaped tube B C D, closed airtight at B by means of a vulcanised india-rubber ring; the tube is fastened in the glass plate E F, and fitted airtight by means of a similar contrivance to the one just mentioned; E F is covered with a cap made of vulcanised caoutchouc, while between B and C a tube is fitted laterally, bent at D, at right angles (this part is not represented in full in the cut) and fitted with a small-bore vulcanised india-rubber tube closed by a spring clamp. The cap and the ring, B, should be touched with some grease. The edges of a beaker can be readily rubbed on a piece of fine-grained and thoroughly smooth and level sandstone, to take off the vitreous glaze, so that a plate of ground glass may fit quite tight thereon; this having been done, the cover E F (a ground-glass plate), may be fitted so tightly that it is possible to keep in the interior of the beaker-glass as good a vacuum as in the receiver of an air-pump.

The filtering-bulb, A (fig. 29), being the most essential portion of this apparatus, its construction requires the greatest possible attention, and should be managed as follows:—Take a glass tube having an inner bore of 2 millimetres, blow at one end a thick bulb (see A, fig. 80), flatten the bulb at the bottom, keep this bulb so hot that the glass is only slightly soft, and while in that condition make holes in it by means of a white-hot steel wire; these holes should be close together and not larger than 0·7 millimetre. The width of the edge, *a b* (fig. 80), differs according to the kind of filtering-paper which it is intended to use. For ordinary filtering-paper the width should be 8 millimetres, for Swedish paper a width of 2 millimetres is sufficient; the perforated glass knob thus obtained is also ground slightly on sandstone. The tube to which the bulb is blown should be so bent as to make the leg B somewhat longer than the leg A; the height of the bulb must not be great; that is to say, it should be sufficiently flat to carry along with the air at the end of the filtration all the liquid into the beaker. The most suitable diameter of the bulb for general use is 2·5 centimetres; the number of holes ought to be 50, but a smaller number will do when the holes are connected together by means of small channels cut in the glass with hydrofluoric acid. The apparatus is connected with an air-pump by a strong india-rubber

tube. The best air-pump is formed by the human lips, but direct experiments have proved that the power of suction of men varies from 10 to 695 centimetres of mercury, that is to say, from $\frac{1}{70}$ to $\frac{2}{10}$ of an atmospheric vacuum. When the operator cannot suck above $\frac{1}{2}$ atmosphere, or when disagreeable gases are to be worked with, the Sprengel pump or the aspirator should be used. Even when full atmospheric pressure is on, the thinnest filtering-paper will not be broken.

In order to use the apparatus the air is pumped out, water being poured simultaneously on A. The rapidity of the current thus called into play effectually removes all impurities, and the water serves also to clean the beaker. This having been done, a circularly-cut piece of filtering-paper, of the same diameter as A, is pressed against A. It

FIG. 29.



remains fixed there, even when the apparatus is blown into; a vacuum is again made while the filtering disc is placed in the solution of the substance to be analysed, care being taken not to let the disc touch the bottom of the vessel in which that solution is contained; as soon as the solution is filtered off from the sediment, some pure water is added, the vacuum being still maintained, after which the apparatus, with the precipitate adhering to it, is removed from the vessel

in which the solution was contained, while any sediment therein remaining is transferred by careful manipulation into a previously-tared crucible.

Fig. 31 exhibits the mode of the connection of the apparatus with the air-pump. The bulb is placed in the vessel, and distilled water added for the purpose of washing the sediment thoroughly, the water running into the beaker (the vacuum being kept on) for the purpose of drying the precipitate by the current of air. This may be carried so far as to cause even gelatinous precipitates to shrink together. The spring clamp now being opened, air is admitted to the beaker, and the filtering-tube removed from the crucible as well as from the cover, E F. If the operation has been properly managed, the disc of filtering-paper remains on the top of the precipitate, the upper surface of the bulb remains clean, while only a very thin and small ring of the substance

adheres to the lower edge of the bulb; this substance is removed by carefully holding a piece of filtering-paper flat in the hand and pressing it gently against the bulb; turn the latter gently so as to rub all the substance on the paper, which, with the substance thus fastened to it, is thrown into the crucible. This having been done, the crucible, covered with its lid, is placed in an air-bath and heated to 105° . At this temperature the precipitate becomes readily and rapidly dry, without any danger of spirting; after which the crucible is ignited, first without the cover, until the very small quantity of paper is consumed, and afterwards with the lid on.

Although a bulb of the size above named is sufficiently large for many substances, it is preferable to have another bulb of 8.5 centimetres diameter for use with such gelatinous precipitates as alumina and iron peroxide. Instead of the platinum crucibles in ordinary use, it is for this purpose preferable, though not indispensable, to use a platinum dish and cover, shaped as shown in fig. 82, and weighing about 28 grammes.

As the rapidity of the operations by this method makes it desirable

FIG. 30.

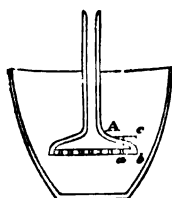
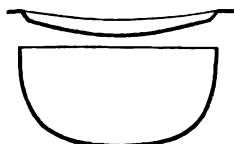


FIG. 31.



FIG. 82.

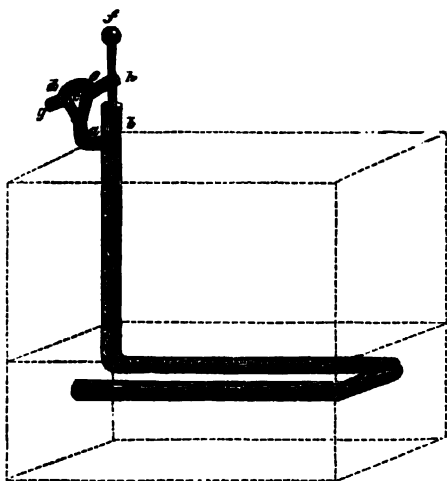


to heat several crucibles at a time to 105° , and since this requires an air-bath with a really good gas-regulator, those hitherto contrived being either of no use or somewhat expensive and too complicated, Dr. Carmichael has contrived the apparatus shown in fig. 83. Anyone who has acquired some practice in glass-blowing may make it for his own use. Take a glass tube 40 centimetres long and 0.6 centimetre interior diameter, bend it as shown in the woodcut so as to admit of two of the bends being placed below the false bottom of the air-bath, and the third, the vertical bend, to pass through an opening out of the bath, but so as not to touch the metal the bath is made of; at *a* a glass tube of 2 millimetres interior diameter is melted on the wider tube, and shaped as shown at *c*; this narrower tube is branched off into 2 parts, each so bent as to be on a level together. At *d* and *e* holes are made in these branches in such a manner as to form small nipples towards the outside, which are next nearly closed, and then connected together by means of an india-rubber tube; the lower end of the wide glass tube is sealed, and the top opening closed with a cork, into which, through a carefully-made hole, a thin and long glass rod is fitted; the cork should extend to *ab*, so as to exclude air. This contrivance is entirely

filled with mercury, and next freed from any adhering air and moisture by heating over a spirit-flame; one of the open tubes at *h* and *g* is in connection with a gas supply-pipe fitted with a tap, the other open glass tube with a burner, while the openings at *d* and *e* are so small that the gas which may pass through them is too small in quantity to heat the bath to any extent, whilst, at the same time, these openings serve to prevent the sudden extinguishing of the flame by the rapid expansion of the mercury.

The apparatus is used in the following manner:—The bath is heated by a gas-burner, until the thermometer connected with the bath indicates nearly the requisite temperature; this having been reached, the glass rod, *f*, is pressed down into the mercury contained in the wider tube, until the mercury at *a* nearly touches the part *c*,

FIG. 33.



which should be made as straight (not rounded) as possible. The sensitiveness of this contrivance depends, of course, upon the quantity of the mercury and its adjustment of surface; but if the apparatus is made with care, according to the directions just described, the bath remains to a fraction of a degree at a constant temperature, even in a draught of air or with a change of pressure of gas. The cooling of the mercury in the narrow tubes prevents oxidation of the metal anywhere in the tube.

The following advantages are obtained by the use of the filtering bulb:—

1. The decantation of liquids is avoided.
2. The washing, ignition, and calculation of the filter-ash is entirely dispensed with. For, since the quantity of ash contained in a filter made of the best paper, and of 12 centimetres diameter, amounts to 0·0005 gramme, the ash contained in a disc of filtering-paper, as used with this apparatus, would only weigh 0·00002 gramme, and even if the paper were of a commoner quality it would make no difference.
3. The velocity of filtration is very great; the water flowing into the beaker in so uninterrupted a current that it appears as if no paper disc were present. When precipitates are to be filtered off, the velocity is somewhat less; but it is then far more rapid than by the ordinary plan, and not less rapid than by Bunsen's method.

4. Since the filtering-tube dips under the fluid, no air can pass through the precipitate until it has been completely washed.

5. When a mineral has been dissolved, or when two substances have to be separated from each other; instead of, as is done by the ordinary method, placing them in a beaker to be further treated, the precipitate by this method remains in the crucible, and can be ignited directly after filtration.

6. This apparatus serves as a filtering-stand, and also as a syphon and pipette.

7. The whole apparatus may be readily kept from dust, and, if required, any gas can be readily admitted to protect a fluid to be filtered from contact with air, while a boiling solution can also be readily filtered.

8. Even so small a quantity of substance as a couple of milligrammes is sufficient for analysis. With so small quantities the entire precipitate remains fixed to the filtering disc, and may be burnt on the lid of a crucible, while any other very small portion of the substance which may adhere to any part of the apparatus may be readily removed and estimated.

9. The use of this apparatus, and the employment of small quantities of substance for analysis, occupy only about one-third of the time as compared with that required for analyses done by the ordinary plan. As an instance of the advantage of employing this method of analysis, the author quotes the following:—A mixture was taken of magnesia, potassium chloride, and common salt, adding thereto some hydrochloric acid so as to convert the magnesia into chloride, expelling any excess of that acid by a gentle heat. The dry saline mass was redissolved in water, and mercury oxide added. The mass was next gently heated in a covered crucible, until all the mercury was volatilised, and the dry residue again treated with water and filtered by means of the filtering-tube above described, by which operation the magnesia was left behind in the crucible. It was then dried in the air-bath and ignited. The solution of the alkalies was next treated in the usual manner with platinum chloride and alcohol, and the potassium platino-chloride, after having been separated from the fluid by the filtering-tube, dried at 105°. The small filtering-paper disc, to which hardly a particle of the salt adhered, was removed, and the potassium platino-chloride, first ignited by itself alone, and afterwards with the addition of the paper disc; the result being that the organic matter of the paper was sufficiently large to cause the reduction of the platinum to the metallic state. The materials left in the crucible were washed with hydrochloric acid to remove any trace of magnesia, and again ignited; the platinum in the filtrate was also reduced to metal, and the sodium chloride present estimated in the usual way, care being taken to remove and estimate the very small quantity of magnesia by means of sodium phosphate, and to deduct the

weight of the magnesia thus estimated from the weight of the sodium chloride.

The results were as follows:—

	Quantities taken	Quantities found
Magnesia . . .	0·0690 grm.	0·0688 grm.
Potassium chloride .	0·1873 „	0·1852 „
Sodium chloride .	0·0876 „	0·0900 „
	<hr/> 0·3439	<hr/> 0·3440

It appears that the magnesium chloride was completely converted into magnesia again, notwithstanding the small loss of this substance due to the solubility of some of it in the alkalies present; that the quantity of the potassium salt found was deficient is accounted for by the fact that the salt was only washed with dilute alcohol, without any addition of ether to lessen the solubility of the potassium platino-chloride. The author analysed twice a portion of a mineral, skolezite, from Scotland, taking in the first case 0·985 gramme of substance, and in the other 0·0807 gramme, the result being that the percentage composition of the substance was found to be:—

	I.	II.
Silica	46·20 .	46·35
Alumina	26·28 .	26·21
Lime	9·22 .	9·17
Soda	5·16 .	5·10
Water	13·25 .	13·45
	<hr/> 100·11	<hr/> 100·28

In reference to the difference of the quantity of water, the author observes that the substance had been kept for several months under a desiccator. It is clear that the principle of the apparatus above described may be applied to qualitative analysis, and also in technology on a larger scale, for which purpose a porcelain plate perforated with small holes may be used with a disc of filtering-paper.

CHAPTER XV.

NEW PROCESSES AND GENERAL METHODS OF MANIPULATION.

An Improved Mode of Filtration.

THE method of filtering, in which Bunsen has availed himself of Sprengel's water-air pump, is a great improvement upon the simple paper system. But the pump is a comparatively costly apparatus, and not always suited to the position and circumstances of a private laboratory, and, as the same, or nearly the same effects can be produced by means which are in every chemist's hands, the plan here proposed may be convenient for some.

The needs of chemists have caused the manufacture of a special paper fitted for most of their filtering operations. But in some cases the texture is too coarse, and in some too fine. When a large-sized filter is used the ash is too uncertain, and too great for nice quantitative operations. A small size requires constant and long-continued attention in order to pass through it even a reasonably small quantity of filtrate, together with the requisite washings.

In a process described by Mr. Isaac B. Cooke, a quantity of carded cotton-wool, so small that the ash in commercial analyses may be generally neglected, will suffice for any ordinary filtration; and a little experience enables the operator, by tight or loose packing, to adopt it to the coarsest or finest precipitate.

A glass flask, of not more than about 800 c.c. content, is fitted with a rubber stopper of soft and smooth surface, and of conical shape, so that the small end easily enters the neck of the flask; but the larger end cannot be forced in even under considerable pressure. Through the centre of the stopper a hole is bored to admit of a glass tube of about $\frac{3}{16}$ inch internal diameter. The tube to be inserted should be about 6 inches long; one end being fused to a very small opening, and the other slightly enlarged in funnel form. About 1 inch of the nearly closed end of the tube is passed through the stopper, fitting tightly; and if an inch traverse the stopper 4 inches will be left outside when the stopper is in its place. Into the funnel-shaped mouth of the tube a small quantity of the carded cotton-wool is packed with the tapering end of a wire not having too sharp a point. The cotton-wool should be lightly pressed in at first until it occupies a length of about $\frac{1}{2}$ to $\frac{3}{4}$ inch of the tube, and then may be pressed

more tightly at the mouth according to the quality of the precipitate to be filtered off, leaving a spreading brush of about $\frac{3}{4}$ inch length projecting from the end.

To put the instrument into operation a small quantity of distilled water is poured into the flask, sufficient, but not more than sufficient, to quite cover the inner convexity of the bottom. The flask is then placed over the lamp till the water boils freely, and all air is expelled from the flask by steam. During the boiling the stopper should be placed in an inclined position, the short end of the tube resting against the inside of the neck of the flask, so as partially to close it but leave space for the air and steam to rush out. Unless the mouth of the flask is thus partially closed during the boiling a much longer time is required to drive out the air; as if quite open a circulation takes place, cold air passing in at one side as steam is driven out at the other.

When steam issues freely past the sides of the stopper, the flask may be taken from the lamp, and the stopper immediately pressed into its place and kept there by pressure until condensation begins. The flask is meantime inverted, and the tube with its brush of cotton-wool plunged into the fluid to be filtered, taking care that the wool is wholly submerged; as if any portion be left dry protruding from the fluid, air will be drawn through it into the flask. As soon as the fluid is seen to be rising up the tube, the apparatus may be reared against a corner and left to itself.

The filtration will proceed with more or less rapidity in proportion as the cotton is packed lightly or solidly into the tube. When all the liquid has been drawn up, and the air is about to follow, a stream of distilled water from the wash-bottle may be driven upon the precipitate to wash it; and as the last portion of this also passes up the washing can be repeated, and again as often as it is thought necessary. Lastly, the air following will leave the precipitate and the cotton-wool in a condition almost dry. The contracted orifice of the inner end of the tube secures it also free from liquid.

It is generally advantageous to perform the filtration from a small porcelain evaporating-basin of about $2\frac{1}{2}$ inches diameter, supported on a cork ring. The fluid and precipitate can be gradually poured and washed into the basin as the process goes on. When it is completed the flask may be reverted, the stopper gently loosened, and the inner end washed by a stream from the wash-bottle into the flask. The cotton plug must now be carefully taken out by forceps over the evaporating-basin, partially wiping the end of the tube in doing so with the clean portion of the plug, and the whole added to the precipitate. The forceps should be carefully wiped with a very small piece of cotton-wool, which may be further used with the forceps to complete the cleaning of the tube, and then also added to the precipitate. The basin, after being rapidly dried over the lamp, is ready for ignition. The precipitate cannot well be separated from the plug

without loss; but there are few cases in which it will be injured by being ignited with the same quantity of cotton of which the plug consists, or, at least, in which that injury cannot be remedied by re-ignition after treatment with nitric or sulphuric acid. On cooling, the basin and its contents can be weighed, and, after brushing out the ash, the basin alone; the difference of course being the weight of the ignited ash.

A flask of 100 to 150 c.c. capacity is usually sufficient for a filtration; but it is not safe to use one larger than 800 c.c. unless it be of a spherical shape without the flat or concave bottom, as larger ones are not always proof against the pressure. A spherical flask would be better also in respect of requiring a smaller quantity of water to drive out the air, and, therefore, also a shorter time to prepare it. In this case, however, if only a small part of the surface of the bottom is covered with fluid, care is required not to crack the flask during the boiling.

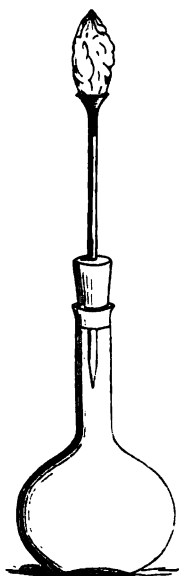
If the stopper be pliable, smooth, and well-fitting, no air will pass between it and the neck of the flask during the operation. But the appearance of such leakage is simulated by the renewed boiling of the fluid in the flask in consequence of the diminished pressure. Unless the fluid has been boiled immediately before filtration, bubbles of air will constantly ascend the tube during the process. Yet the vacuum caused by the initial boiling will be so nearly completed that the filtration and washing may be continued if necessary till the body of the flask is nearly filled with fluid, and on reversion only a portion of the neck will be occupied with air.

When a flask is found unexpectedly not to be large enough to contain all the fluid required by the washing, it is better to suspend the filtration before the flask is full, raising it out of the fluid to allow air to pass up the tube before reverting. The plug will then be in a dry state, and no portion of the fluid will run down the outside of the tube and be lost. Another flask in which the same stopper fits may be prepared by boiling, the tube inserted, and the filtration completed.

Separation and Subsequent Treatment of Precipitates.

Mr. F. A. Gooch, impressed with the desirability of further improvement in those processes of quantitative analysis which involve the use of dried filters, or the separation of filter and precipitate before ignition, has had the good fortune to succeed in devising and preparing a felt of anhydrous asbestos, which is capable of filtering liquids

FIG. 34.



with a rapidity and efficiency at least as great as may be obtained by the use of good filter-paper. It is light, compact, incombustible at the highest temperatures used in analytical processes; is not acted upon by acids (excepting hydrofluoric acid) or alkalies; is sufficiently coherent to resist entirely the disintegrating action of a liquid forced through it under the pressure of the Bunsen pump, and may, moreover, be prepared by a very simple process; it is, in short, a filtering material which makes it possible to reach a high degree of accuracy in many analytical processes which hitherto have been none of the best, and to add to those already known new methods which previously have been impracticable. The mode of preparing and using the asbestos felt is as follows:

First.—White, silky, anhydrous asbestos is scraped to a fine short down with an ordinary knife-blade, boiled with hydrochloric acid to remove traces of iron or other soluble matter, washed by decantation, and set aside for use.

Secondly.—A platinum crucible of ordinary size, preferably of the broad low pattern (fig. 85), is chosen, and the bottom (fig. 86) perforated

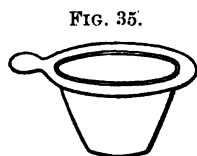


FIG. 35.

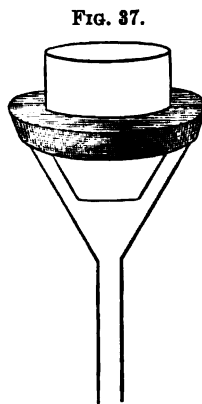
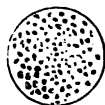


FIG. 37.

FIG. 36.



with fine holes (the more numerous and the finer the better) by means of a steel point; or, better still, the bottom may be made of fine platinum gauze. Next a Bunsen funnel of the proper size is selected, and—following Munroe's plan for holding his porous cones—over the top a short piece of rubber tubing is stretched and drawn down until the portion above the funnel arranges itself at right angles to the direction of the stem. Within the opening in

the rubber, the perforated crucible is fitted as shown in fig. 37, and the funnel is connected with the receiver of a Bunsen pump or other exhausting-apparatus in the ordinary manner.

To make the asbestos felt, the pressure of the pump is applied and a little of the asbestos prepared as described, and, suspended in water, is poured into the crucible. The rubber and the crucible are held together by the pressure of the vacuum-pump with sufficient force to make an airtight joint; the water is drawn through, and the asbestos is deposited almost instantly in a close compact layer upon the perforated bottom; more asbestos (if necessary), in suspension as before, being poured upon the first until the layer becomes sufficiently thick or the purpose for which it is intended. Finally, a little distilled

water is drawn through the apparatus to wash away any filaments that might cling to the under side, and the filter is ready for use: the whole process occupying scarcely more time than is necessary to fold and fit an ordinary paper-filter to a funnel.

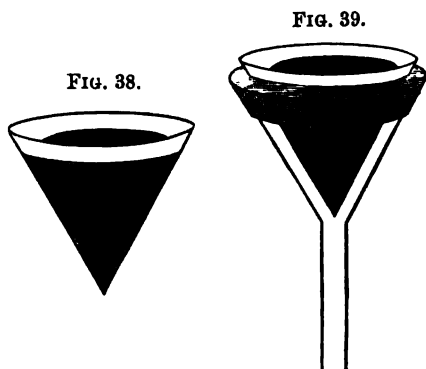
To prepare the filter for the estimation of a precipitate, the crucible, with the felt undisturbed, is removed from the funnel and ignited. In case the precipitate to be subsequently collected must be heated to a very high temperature for a long time, it is better to enclose the perforated crucible with its felt within another crucible; because in such cases asbestos felt is apt to curl at the edges, and without such precaution some of the precipitate might drop through the perforations and be lost. For drying at low temperatures, however, and even for ordinary ignitions, a second crucible is unnecessary; but during the ignition of an easily reducible substance care must be taken to prevent the contact of unburnt gas with the perforated bottom.

To perform the filtration, the crucible is replaced in the funnel, the pressure applied, and the process conducted precisely as in an ordinary filtration by the Bunsen pump. It is necessary to observe that the vacuum-pump is to be started before pouring the liquid upon the filter. The final drying or ignition, as the case may be, of precipitate and filter is made without difficulty or need of extra precaution.

When turbid liquids are to be filtered, or gelatinous precipitates to be separated, instead of the perforated crucible, it is better to use a platinum cone (figs. 38 and 39), the upper part of foil (to make a tight joint with the rubber fitting of the funnel), the lower of gauze. The method of covering the gauze with felt is identical with that described above. By reason of the larger filtering-surface of this apparatus, the tendency to become clogged is, of course, very much diminished. When subjected to prolonged ignition, the gauze cone is enclosed within a crucible or a cone of platinum foil.

In operations in which platinum is liable to receive injury, a porcelain crucible with a perforated bottom may be used; but recourse to this is rarely necessary, particularly when one may use the gauze cone, protected as it is by asbestos felt; moreover, the perforation of porcelain with numerous fine holes is a matter of considerable difficulty and expense.

Asbestos felt may be also used in the process of reverse filtering,



it being merely necessary to dip the platinum rose into the asbestos mixture, after starting the vacuum-pump, in order to make the felt. The rose, with the felt attached, and the vessel in which the precipitate is collected are to be weighed together, both before and after filtration.

Nothing can be simpler than the whole method of preparation and use of the apparatus which has been described, and its efficiency is extremely great. Clean water may, under the pressure of a Bunsen pump, be passed through a gauze cone coated with asbestos felt, which exposes a filtering surface of 24 square centimetres (nearly the same as that of a paper-filter, 8 centimetres in diameter, when folded in the ordinary manner), with ease at the rate of a litre per minute.

When the filtering-surface is less, the rapidity of filtration is, of course, somewhat diminished, but always exceeds that of paper of the same dimensions. When the felt is deposited upon gauze, the layer may be surprisingly thin and yet be efficient enough for all ordinary purposes. If the layer of felt be thick, the filtrate from barium sulphate freshly precipitated in the cold may be made to pass through clear. But the great superiority of asbestos felt lies in its constancy of weight, whether dried at high or low temperatures, the rapidity with which it may be safely and completely dried, and its refractoriness as regards acids (excepting hydrofluoric acid) and alkalis.

Separation of Minerals for Analysis.

Mr. E. Sonstadt avails himself for this purpose of their different specific gravities. He prepares a heavy liquid (sp. gr. 3.01) with a solution of mercuric iodide in potassium iodide, by adding alternately those salts in a dry state to the solution, until no more of either is dissolved. The free iodine which sometimes colours it is then removed by means of a crystal or two of sodium thiosulphate, and the liquid, which possesses a very high density, then presents a light straw colour.

The roughly-crushed mineral is thrown into the solution, when any ingredients heavier than 3.01 sink, whilst the lighter ones float. Each class can thus be collected separately, and requires merely to be washed in distilled water. The solution may be diluted if required.

On the Incineration of Filters.

A previous complete drying of the precipitate is not merely a loss of time, but a disadvantage, whilst introducing the still moist precipitate into the crucible requires the application of a very gentle heat at the outset, and thus ensures the most favourable conditions for the easy and complete incineration of the filter-paper. Precipitates not washed upon the filter-pump can be readily brought to a sufficient degree of dryness if laid for a short time upon blotting-paper or unglazed earthenware.

Dry filters may be also much better incinerated after previous charring at the lowest possible temperature, than by rapid carbonisation or direct ignition in the flame. How advantageous it is to char previously very slowly may best be seen on incinerating filters, whose contents impede the complete combustion of the paper by the old process, e.g. silicic acid, magnesium-ammonio phosphate, &c. Charred paper obtained by rapid heating is deep black and of a silky lustre, whilst if slowly carbonised it is brownish black, dull, and smoulders away like tinder. Charred paper of the first kind appears under the microscope perfectly amorphous, whilst the other displays the carbonaceous skeleton of the fibre.

A careful removal of precipitates from the filter—with the exception of cases like zinc and cadmium, where volatile reduction-products may be formed—is quite useless, since the errors which it was hoped to obviate are not really avoided. On incineration with the filter, wet or dry, an error due to reduction may be easily corrected, e.g., in barium sulphate with sulphuric acid; in lead sulphate with nitric and sulphuric acids; in iron and copper oxides with nitric acid; in silver chloride with nitric and hydrochloric acids, &c.

Indicators for Alkalinity.

The comparative sensitiveness of litmus, methyl-orange, phenacetoline and phenol-phthaleine has been carefully studied by Mr. R. T. Thomson. In the absence of all interfering agents, litmus and methyl-orange are equally sensitive; phenacetoline and phenol-phthaleine about five times more sensitive.

If soda exists as hydrate along with sodium carbonate, phenacetoline and phenol-phthaleine are not suitable, if the proportion of carbonate is large.

For ammonia phenol-phthaleine is useless, as it does not distinctly indicate the end of the reaction.

In the estimation of alkalies existing as carbonates and bicarbonates, the well-known fact is mentioned that litmus cannot be used for the estimation of ammonia in the commercial carbonate without adding excess of acid, boiling to expel carbonic acid, and titrating back with an alkali. The same holds good for phenacetoline. Methyl-orange appears to have given an apparent excess of ammonia. Phenol-phthaleine is useless for ammonium carbonate, and requires tedious boiling with the carbonates of the fixed alkalies.

In presence of alkaline sulphates, nitrates, and chlorides, litmus and phenacetoline are as delicate as in their absence. With methyl-orange a greater quantity of normal acid is needed to bring out the full pink colour than if distilled water only were present. Phenol-phthaleine is unaffected by the above-named salts in case of potash and soda, but ammonia and its salts must be carefully excluded if this indicator is to be used.

If the alkaline sulphites are present, the results given by all the indicators are vitiated.

Sodium thiosulphate is neutral to all the indicators.

With sodium sulphide, litmus, methyl-orange, and phenacetoline gave accordant results; phenol-phthaleine showed one half too little Na_2S , unless boiled, when it approached the truth.

If alkaline phosphates were present, methyl-orange gave results slightly higher and nearer the truth than litmus, the end of the reaction being more distinct. Phenol-phthaleine cannot be depended upon. If phenacetoline is used, the normal acid must be added until a permanent colour is produced, when the results agree with those obtained with litmus.

If sodium silicate is present, litmus, methyl-orange and phenacetoline give results which do not materially differ. With phenacetoline the end reaction is indistinct. Phenol-phthaleine gives results considerably too low.

With sodium aluminate litmus gives too high a result, and an indistinct termination: with methyl-orange the result is much too high, whilst phenacetoline and phenol-phthaleine give a correct estimation.

Potassium nitrite is neutral to litmus, phenacetoline, and phenol-phthaleine; methyl-orange is not admissible.

For the estimation of soda in borax, methyl-orange shows a correct result, and the end of the reaction is quite distinct. With litmus and phenacetoline the end is indistinct, and phenol-phthaleine is utterly useless.

On the estimation of the mineral acids with a caustic alkali, it need only be said that ammonia must not be used with phenol-phthaleine. Sodium carbonate can be used in the cold with methyl-orange. If phenacetoline is to be employed, a little carbonate must be used along with the caustic alkali.

For free oxalic acid, litmus and phenol-phthaleine give distinct and concordant results, whilst methyl-orange and phenacetoline cannot be recommended.

For free acetic acid, methyl-orange and phenacetoline are not well adapted. With litmus the end of the reaction is not easily recognised. Phenol-phthaleine works admirably.

For tartaric acid the results are similar, phenol-phthaleine showing the most distinct reaction.

With citric acid, limejuice, &c., the case is similar, methyl-orange and phenacetoline being useless, and phenol-phthaleine giving a sharper end reaction than litmus.

For estimating caustic alkalies in presence of alkaline carbonates, and quicklime in presence of calcium carbonate, Dr. Lunge recommends a method first suggested by Degener.

The solution of lime is coloured with phenacetoline, and normal

acid is dropped in as long as the yellowness produced by each drop at once gives place to redness. If this change does not occur for a few seconds, the burette is read off, and two more drops of acid are added. If the liquid remains yellow, the former reading was correct, but if it becomes red, the addition of the acid must be continued until a permanent yellow colouration is established.

The estimation of caustic soda is effected directly by titration with acid, using phenacetoline as indicator. As soon as the liquid remains of a faint rose colour all the sodium hydroxide is saturated, and only the carbonate remains. If more acid is added the yellowish red colouration changes suddenly to a golden yellow. At this point the carbonate also is saturated. The process is most suitable for caustic lyes which contain moderately large proportions of carbonate. Ammonia behaves differently from caustic soda, and is at once reddened by phenacetoline.

Dr. Lunge recommends practice with this indicator with liquids of known composition, so as to acquire a knowledge of the correct shade of colour.

Ultramarine Test-Paper.—The great sensitiveness of artificially-made ultramarine for even very weak acids has been turned to account by applying that pigment to prepare a test-paper especially suited for the rapid detection of the presence of free acids in such salts as aluminium sulphate, alum, and other similar compounds. The ultramarine intended for this use should be that known commercially as No. 1; it should first be mixed with some water collected on a filter, and then thoroughly washed with some boiling distilled water, and afterwards incorporated with a mucilage made of 1 part of selected Irish moss, previously washed with cold water, boiled with about 80 parts of distilled water; the pigment thus obtained is uniformly painted over best filtering-paper, and, after drying, cut up into strips, as is usual for litmus-paper, and preserved in a glass-stoppered bottle. In order to test the ultramarine, it is necessary to prepare a perfectly neutral alum in the following manner. Alum of commerce, by preference potash alum, is dissolved in from 8 to 10 times its weight of boiling water, and this solution is poured into twice its bulk of alcohol at 80 per cent. The alum separated after complete cooling is collected, redissolved in boiling water, and the solution again poured into the same quantity of fresh alcohol of the same strength; the alum which separates on cooling is collected on a filter, and, after having been washed with alcohol, dissolved in water; a drop or two of this solution should not discolour the ultramarine, while its almost instantaneous discolouration should follow on its being touched with a drop or two of very dilute sulphuric acid, 1 part of strong acid to from 50 to 60 parts of distilled water.

Application of Hydrogen Peroxide in Chemical Analysis.

The behaviour of hydrogen peroxide with ammonium sulphide, or of hydrogen sulphide with ammoniacal hydrogen peroxide, may be used qualitatively for the detection of these compounds, and quantitatively for estimating hydrogen sulphide, whether gaseous or in solution, and for estimating the sulphur or the metal in metallic sulphides. In cases where the sulphide can be decomposed by the direct action of hydrogen peroxide in presence of ammonia, it takes place in this manner; in other cases, as in the sulphides which on heating with hydrochloric acid evolve definite quantities of sulphuric acid, it takes place by conversion into sulphuric acid or barium sulphate. Just as hydrogen sulphide or metallic sulphides are oxidised to sulphuric acid or to sulphate, sulphurous acid and sulphites are oxidised to sulphuric acid or sulphates. These reactions may be utilised in various directions.

Several metallic sulphides are completely oxidised by ammoniacal hydrogen peroxide without the formation of precipitates, as the arsenic, copper, zinc, and thallium sulphides. After the expulsion of the ammonia all the copper is deposited by a copper solution as a dirty green precipitate, not changed by ignition. From the zinc solution only a part of the zinc is separated as a white deposit. On the action of hydrogen peroxide upon antimony trisulphide a part of the antimony separates as a white precipitate, whilst the liquid contains all the sulphur as sulphuric acid. Tin sulphide is decomposed in a similar manner, oxide being deposited and the sulphur oxidised to sulphuric acid. With the other metallic sulphides the behaviour of hydrogen peroxide is very various. It attacks mercury sulphide, which is scarcely affected by nitric acid, very energetically. After the expulsion of the mercury there remains a spongy precipitate which settles quickly, dissolves in hydrochloric acid, and is converted into a white powder by the action of nitric acid. After the conversion of mercury sulphide by the action of hydrogen peroxide, no mercury can be detected in the filtrate. Cadmium sulphide is decomposed with formation of a yellowish-white precipitate, easily soluble in hydrochloric acid. When the oxidation is completed a part of the cadmium remains in the filtrate as sulphate.

Certain metallic sulphides, the solutions of which in acids are precipitable by ammonia, are decomposed by hydrogen peroxide with formation of sulphuric acid and separation of hydroxides; thus iron sulphide, which is oxidised as just mentioned, and manganese sulphide, which is quickly and completely decomposed with formation of sulphuric acid and separation of a mixture of hydrated peroxide and oxide. On heating cobalt sulphide with ammoniacal hydrogen peroxide there is first formed soluble cobalt sulphate, which on prolonged heating is further attacked with formation of a dirty brown precipitate. Nickel sulphide is decomposed in the same manner, with formation of a

green precipitate which does not contain all the nickel. Silver and bismuth sulphides are not attacked by ammoniacal hydrogen peroxide; lead sulphide is readily converted into sulphate.

The property of hydrogen peroxide in alkaline solution, of easily and completely oxidising hydrogen sulphide to sulphuric acid, may be used, in the first place, for the estimation of hydrochloric, hydrobromic, and hydriodic acids in liquids containing hydrogen sulphide. These estimations have occasioned much trouble to analysts.

From the estimation of hydrochloric acid along with hydrogen sulphide an ammoniacal solution of hydrogen peroxide is added, and the mixture is boiled until no more bubbles of oxygen rise up. Nitric acid and silver nitrate are then added, and the silver chloride is estimated in the usual manner.

For hydriodic acid in presence of hydrogen sulphide the procedure is similar, but the hydrogen peroxide is used mixed not with ammonia, but with sodium carbonate. The mixture is boiled as before, and silver nitrate is added, and nitric acid until a faintly acid reaction is produced.

In estimating hydrobromic acid under similar circumstances the process is exactly the same as for hydriodic acid.

In the metallic sulphides capable of direct oxidation by hydrogen peroxide the quantity of metal can be calculated from the sulphuric acid formed. This method is applicable to the sulphur compounds of arsenic, antimony, zinc, copper, and cobalt. The sulphide is dissolved in ammonia, treated with sufficient hydrogen peroxide, boiled to expel excess, the liquid is acidulated with hydrochloric acid, and the sulphuric acid precipitated with barium chloride.

Antimony trisulphide is treated exactly like arsenic trisulphide. Antimony pentasulphide is incompletely oxidised by hydrogen peroxide.

Sulphides which dissolve by boiling with hydrochloric acid, with liberation of hydrogen sulphide, can be readily and accurately estimated by converting the latter compound into sulphuric acid.

Sodium thiosulphate is decomposed on boiling with hydrochloric acid, sulphur being deposited and sulphur dioxide formed. This method permits of the estimation of sodium thiosulphate, sulphite, and sulphate, when occurring together. The weighed substance is decomposed in the apparatus by means of hydrochloric acid, the sulphur dioxide corresponding to the sulphite and thiosulphate is estimated, the sulphur remaining in the flask is weighed on a tared filter, and the sulphuric acid in the filtrate is precipitated as barium sulphate. From the quantity of the sulphur that of the thiosulphate is calculated.

On the Preservation of Platinum Crucibles.

In connection with some sensible remarks upon the use of sand in cleaning platinum crucibles—a practice which, with Berzelius,¹ he

¹ *Lehrbuch der Chemie*, 1841, 4th Aufl., p. 516.

heartily commends, urging that it should be employed every time that a crucible is used—Erdmann explains the cause of the grey coating which forms upon platinum crucibles whenever they are ignited in the flame of a Bunsen gas-burner.

This coating has given rise to much annoyance and solicitude among chemists. Indeed, it has often been asserted that the use of Bunsen's burner is unadvisable in quantitative analysis, since by means of it the weight of platinum crucibles is altered and the crucibles themselves injured. The coating is produced most rapidly when the crucible is placed in the inner cone of the flame, and the more readily in proportion as the pressure under which the gas is burned is higher. Having found it advantageous to maintain, by means of a special small gas-holder, a pressure of 4 or 5 inches upon the gas used in his own laboratory, Erdmann has observed that the strong gas-flame thus afforded immediately occasions the formation of a dull ring upon the polished metal placed in the inner flame, this ring being especially conspicuous when the crucible becomes red-hot; it increases continually, so that after long-continued ignition the whole of the bottom of the crucible will be found to be grey and with its lustre dimmed.

This ring is caused neither by sulphur, as some have believed, nor by a coating of inorganic matter, but is simply a superficial loosening of the texture of the platinum in consequence of the strong heat; whence it first of all appears in the hottest part of the flame.

In conjunction with Pettenkofer, Erdmann instituted several experiments which have left but little doubt that the phenomenon depends upon a molecular alteration of the surface of the metal. If a weighed polished crucible be ignited for a long time over Bunsen's lamp, the position of the crucible being changed from time to time in order that the greatest possible portion of its surface shall be covered with the grey coating, and its weight be then estimated anew, it will be found that this has not increased. The coating cannot be removed either by melting with potassium bisulphate or with sodium carbonate. It disappears, however, when the metal is polished with sand; the loss of weight which the crucible undergoes being exceedingly insignificant, a crucible weighing 25 grammes having lost hardly $\frac{1}{2}$ a milligramme. When the grey coating of the crucible is examined under the microscope it may be clearly seen that the metal has acquired a rough, almost warty surface, which disappears when it is polished with sand. Platinum wires which are frequently ignited in the gas-flame—for example, the triangles which are used to support crucibles—become, as is known, grey and brittle. Under the microscope they exhibit a multitude of fine longitudinal cracks, which as the original superficial alteration penetrates deeper, become more open, or as it were spongy, until, finally, the wire breaks.

If such a wire is strongly and perseveringly rubbed with sand the cracks disappear, and the wire becomes smooth and polished; for the

grains of sand, acting like burnishers, restore the original tenacity of the metal, very little of its substance being rubbed off meanwhile. The loosening effect of a strong heat upon metals is beautifully exhibited when silver is ignited in the gas-flame, a thick polished sheet of silver immediately becoming dull white when thus heated. Under the microscope the metal appears swollen and warty. Where it has been exposed to the action of the inner flame along its circumference, this warty condition is visible to the naked eye. A stroke with the burnishing-stone, however, presses down the loosened particles and reproduces the original polish. This peculiar condition which the surface of silver assumes when it is ignited is well known to silversmiths; it cannot be replaced by any etching with acids; and it must be remembered that what is dull white in silver appears grey in platinum.

If each commencement of this loosening is again destroyed, the crucibles will be preserved unaltered; otherwise they must gradually become brittle. Crucibles of the alloy of platinum and iridium are altered like those of platinum when they are ignited. It is, however, somewhat more difficult to reproduce the original polish of the metal by means of sand, as might be expected from the greater hardness of the alloy.

The sand used should be well worn. When examined under the microscope no grain of it should exhibit sharp edges or corners; all the angles should be obtuse.

Electrolytic Methods of Analysis.

The electrolytic behaviour of thallium, iridium, vanadium, palladium, molybdenum, selenium, and tellurium has been examined by L. Schucht. He finds that thallium is not deposited under the influence of the current from a solution of the sulphate or nitrate containing free acid. The precipitation from a neutral solution is also incomplete, owing to the liberation of gas. From an ammoniacal solution lead-grey metallic thallium is deposited at the negative electrode, with a strong escape of gas, and blackish-brown thallium oxide at the positive electrode. The result is the same in a solution of thallium supersaturated with potash. From alkaline solutions the precipitation is complete.

Iridium is deposited as a bluish-white metal at the negative electrode if the sulphate is submitted to electrolysis. With solutions containing organic acids iridium is also deposited in a firmly-adherent state, with abundant escape of gas.

On the electrolysis of vanadium chloride dissolved in water containing hydrochloric acid there is no precipitation. The blue colour of the solution changes to green and violet, the vanadic acid being reduced to vanadous oxide.

An aqueous solution of palladious nitrate, acidified with a few drops of nitric acid, gives, immediately on closing the circuit, a

bronze-coloured deposit at the negative pole, which ultimately appears black. At the positive pole there appears a slight deposit of oxide of a red colour. In alkaline solutions of palladious oxide the precipitation is much slower, and oxide also appears.

From the ammoniacal solution of molybdic acid molybdous oxide is deposited. Coloured rings appear at the negative pole; they become denser and take a deep blue-black colour. The precipitation is accompanied with a free escape of gas, and is complete. The deposit adheres very firmly. In acid solutions there is no precipitation.

Selenium is deposited both from acid and alkaline solutions at the negative pole, at first as a light brownish-red coating, which gradually becomes thicker and darker. The precipitation is perfect. As the deposit does not adhere firmly to the platinum cone, Schucht oxidizes the selenium by boiling with nitric acid, and adds the solution of some salt the metal of which is thrown down by the current in a solid form, and thus obtains a firmly-adhesive deposit of selenium. He prefers for this purpose a solution of copper. The positive pole is covered with a dark coating which dissolves in hydrochloric acid with a yellow colour. The author ascribes this precipitation to the action of hydrogen selenide.

Tellurium behaves similarly to selenium, but is much more easily reduced by electrolysis.

Analysis of the Gold and Platinum Salts of Organic Bases.

M. C. Scheibler dissolves a weighed quantity of the acid or platinum salt in water, or if it does not happen to be readily soluble, keeps it suspended therein, and places it in contact with metallic magnesium, whereby the metals gold and platinum are separated, and hydrogen is at the same time evolved. This operation is carried on at the ordinary temperature, or if the salts are difficultly soluble, on a water-bath; the fluid may be acidified, but not with hydrochloric acid, since the object often may be to estimate chlorine also. The ribbon-like magnesium wire met with in commerce is sufficiently pure for this purpose. The gold and platinum separated during this operation are, by means of careful decantation, freed from the fluid wherein they are immersed, and next transferred to a filter and washed, first with distilled water, and next, after the filtrates intended for the estimation of chlorine have been set aside, with dilute hydrochloric acid, in order thereby to remove any excess of magnesium or any magnesia which might remain mixed with or adherent to these metals; after having been well purified and dried the metals are ignited and weighed. The results obtained by this method are very correct.

To Prevent the Bumping of Boiling Liquids.

In cases where the introduction of any foreign matter into the liquid about to be distilled is undesirable, Dr. Hugo Müller, F.R.S., introduces through the cork in the tubulure of the retort a glass tube, which is drawn out to a long capillary tube and pressed tightly to the bottom of the retort. The upper end of the glass tube is connected, by means of an india-rubber tube, with a generator of carbonic acid, or hydrogen, or a gas-holder containing air, and whilst the distillation is going on, one of these gases is passed in a slow but continuous current through the liquid. Under these conditions, all bumping is avoided, and the distillation proceeds with the utmost facility.

For ordinary purposes, however, it is still more convenient to introduce into the liquid about to be distilled a small fragment of sodium amalgam or, in cases where the liquid is acid, a small piece of sodium-tin. Methylic alcohol is well known to be one of the most difficult liquids to distil; yet, on the introduction of a minute piece of sodium amalgam or sodium-tin, it can be distilled without the slightest inconvenience. On one occasion Dr. Müller found that more than 400 grammes of methylic alcohol distilled over with perfect steadiness, and without exhausting the activity of a fragment of sodium-tin, weighing not more than 0.06 gramme.

It is, perhaps, hardly necessary to mention that the action of sodium amalgam and sodium-tin is due to a minute but continuous disengagement of hydrogen taking place during the process of distillation.

On the Correct Adjustment of Chemical Weights.

The following description of the method adopted for adjusting a set of platinum weights is taken from the author's Memoir on the Atomic Weight of Thallium.¹

A set of weights as ordinarily supplied by even the best instrument-makers is never absolutely exact; however carefully they may be adjusted, the pieces of metal which respectively represent 1000 grains, 100 grains, 10 grains, &c. are only more or less approximations to the true weights. In most chemical analyses, the error arising from such inaccuracies in the weights used is so small, in comparison to errors of manipulation or to imperfections inherent in the chemical processes adopted, that it may generally be disregarded; but when the chemist has for his object the estimation of an atomic weight, or is engaged in other researches demanding the highest refinement of accuracy which chemistry and physics can supply, then he is bound to neglect no correction which will increase the precision of the results. That chemists whose well-trained reasoning powers allow

¹ *Phil. Trans.* 1873, p. 277.

them to take for granted nothing which is not capable of experimental verification, and who insist upon the utmost attainable precision in their balances, should, as a rule, neglect the probable errors which the inaccuracies of their weights may introduce, is somewhat inconsistent.

The weights employed in the experiments were of platinum. The platinum was quite pure; it was fused, cast, and then well hammered. The weights were adjusted by myself during May, June, July, and August, 1864: they were first roughly adjusted, and then the specific gravity of each weight was taken. The weights were heated to redness in a bath of magnesia previous to ascertaining their specific gravity. The density of the larger weights was ascertained to the second place of decimals, and that of the smaller ones to the first place. The record of the final adjustment of these weights will be sufficient to show the method adopted.

In taking the specific gravity of the weights, the distilled water was contained in a glass beaker of about 250 cubic inches capacity. Each weight was suspended by a fine platinum wire to be attached to the pan of the balance. With this wire affixed the weight was introduced into a small glass vessel filled with water, and heated over a spirit-lamp to the boiling-point. When all the air-bubbles had been expelled by this process, the small jar containing the weight was lowered into the water in the beaker; the weight, on removing the small jar, being perfectly free from any adhering bubbles of air. After the temperature had sunk to the proper point, the specific gravity was taken.

The 1000-grain weight was selected as the standard: for in nearly every process in which weights are used in chemistry, the object is not to ascertain the *absolute* weight of a substance in terms of a grain or gramme, but to estimate its *relative* weight in comparison with that which it possessed at some other time before it was submitted to certain analytical or synthetical operations. If the weighings are performed with the same weights, it does not at all matter whether the weights are absolutely of the value which they profess to be; but it is very important that they should bear a known proportion to each other. This must be understood as referring only to ordinary chemical research in synthesis or analysis. In many physical investigations it is of great importance that the 1000-grain weight should really represent 1000 normal grains, or that its deviation from that value should be accurately estimated; but I confess I do not know where a standard weight suitable for such a comparison is to be met with. The weights at first tried were far from accurate among themselves. I accordingly ascertained their errors by the method described below, and then adjusted them myself according to the corrections thus found necessary. The residual errors in the weights were then finally taken in the following manner:

The balance being brought into equilibrium and the temperature

and barometrical pressure carefully noted, the 1000-grain weight was placed in the left pan, and in the right the 600, the 300, and the 100-grain weights. It was now found that, to bring the balance back to equilibrium, a slight additional weight had to be placed on the right side to supplement the three weights already in that pan. This was noted. The weights were then removed to the opposite sides, the 1000-grains being on the right and the three smaller weights on the left. It was now found that a small weight had to be subtracted from the side carrying the three weights in order to produce equilibrium. The weights were removed and interchanged in this manner ten times, so as to eliminate, as far as possible, the errors arising from observation, or the unequal expansion by heat of the arms of the balance; and by applying the method of least squares to the results obtained, the following equation was arrived at:

$$(1000) = (600) + (300) + (100) + 0.01 \dots a,$$

the figures within parentheses representing the nominal value of the actual pieces of platinum stamped 1000, 600, 100 grains, &c.

In a similar manner the values of the remaining weights were ascertained; thus:

$(600) = (300) + (200) + (100)$	+	0.00777	.	.	.	<i>b</i> .
$(300) = (200) + (100)$	+	0.00991	.	.	.	<i>c</i> .
$(200) = (100) + (60) + (80) + (10)$	+	0.01577	.	.	.	<i>d</i> .
$(100) = (60) + (30) + (10)$	-	0.00080	.	.	.	<i>e</i> .
$(60) = (30) + (20) + (10)$	-	0.00522	.	.	.	<i>f</i> .
$(30) = (20) + (10)$	+	0.00154	.	.	.	<i>g</i> .
$(20) = (10) + (6) + (8) + (1)$	+	0.00355	.	.	.	<i>h</i> .
$(10) = (6) + (3) + (1)$	+	0.00052	.	.	.	<i>i</i> .
$(6) = (3) + (2) + (1)$	-	0.00102	.	.	.	<i>j</i> .
$(3) = (2) + (1)$	+	0.00165	.	.	.	<i>k</i> .
$(2) = (1) + (.6) + (.8) + (.1)$	-	0.00312	.	.	.	<i>l</i> .
$(1) = (.6) + (.8) + (.1)$	-	0.00508	.	.	.	<i>m</i> .
$(.6) = (.3) + (.2) + (.1)$	-	0.00260	.	.	.	<i>n</i> .
$(.8) = (.2) + (.1)$	+	0.00225	.	.	.	<i>o</i> .
$(.2) = (.1) + (.06) + (.03) + (.01)$	-	0.00100	.	.	.	<i>p</i> .
$(.1) = (.06) + (.03) + (.01)$	-	0.00802	.	.	.	<i>q</i> .
$(.06) = (.03) + (.02) + (.01)$	-	0.00607	.	.	.	<i>r</i> .
$(.03) = (.02) + (.01)$	-	0.00642	.	.	.	<i>s</i> .
$(.02) = (.01) + (.01r)^1$	-	0.00118r	.	.	.	<i>t</i> .
$(.01) = (.01r')$	+	0.00413r'	.	.	.	<i>u</i> .
$(.01) = (.01r'')$	+	0.00410r''	.	.	.	<i>v</i> .

We have now the data for ascertaining the absolute values of the weights in terms of the (1000) weight taken as standard. Adding the equations *a* and *b* gives

$$(1000) = 2(300) + (200) + 2(100) + 0.01777.$$

Multiplying equation *c* by 2 gives

$$2(300) = 2(200) + 2(100) + 0.01982.$$

¹ *r*', *r*'' represent riders, two of which were adjusted in this manner.

Subtracting e from d gives

$$(200) = 2(100) + 0.01607.$$

Now by $(a + b) + 2c + 3(d - e)$ we get

$$(1000) = 10(100) + 0.01777 + 0.01982 + 0.04827;$$

$$\therefore (1000) = 10(100) + 0.0858;$$

$$\therefore \left(\frac{1000}{10}\right) = (100) + 0.00858;$$

$$\therefore (100) = 100 - 0.00858;$$

$$\therefore (100) = 99.99142 \text{ grains} \quad . \quad . \quad . \quad \text{A.}^1$$

Substituting this value for the (100) weight, we get from equation c ,

$$99.99142 = (60) + (30) + (10) - 0.0003;$$

$$\therefore (60) + (30) + (10) = 99.99172 \quad . \quad . \quad . \quad \text{B.}$$

From equation d we therefore get

$$(200) = 99.99142 + 99.99172 + 0.01577;$$

$$\therefore (200) = 199.99891 \quad . \quad . \quad . \quad . \quad \text{C.}$$

From equation c we get

$$(800) = 199.99891 + 99.99142 + 0.00991;$$

$$\therefore (800) = 800.00024 \quad . \quad . \quad . \quad . \quad \text{D.}$$

From equation b we get

$$(600) = 800.00024 + 199.99891 + 99.99142 + 0.00777;$$

$$\therefore (600) = 599.99834 \quad . \quad . \quad . \quad . \quad \text{E.}$$

Again, adding e and f ,

$$(100) = 2(30) + 2(10) - 0.00552;$$

\therefore from A,

$$99.99142 = 2(30) + 2(10) - 0.00552.$$

Multiplying g by 2,

$$2(80) = 2(20) + 2(10) + 0.00808.$$

Subtracting i from h ,

$$(20) = 2(10) + 0.00808.$$

By adding e , f , twice g , and thrice the last equation, we get

$$99.99142 = 10(10) + 0.000665;$$

$$\therefore (10) = 9.998477 \quad . \quad . \quad . \quad . \quad \text{F.}$$

From equation i we get

$$9.998477 = (6) + (3) + (1) + 0.00052;$$

$$\therefore (6) + (3) + (1) = 9.997957. \quad . \quad . \quad . \quad \text{G.}$$

Substituting these values in h , we get

$$(20) = 9.998477 + 9.997957 + 0.00855;$$

$$\therefore (20) = 19.999984 \quad . \quad . \quad . \quad . \quad \text{H.}$$

From g we get

$$(30) = 19.999984 + 9.998477 + 0.00154;$$

$$\therefore (30) = 29.999991 \quad . \quad . \quad . \quad . \quad \text{I.}$$

¹ Although these decimals are carried to the sixth place, the balance would not indicate beyond the fourth place. By taking the mean of ten interchanged weighings, I could obtain a fifth place. The calculated values of the weights were carried to a sixth decimal, in order to avoid inaccuracy in the fourth and fifth places when several values were summed.

From f we get

$$(60) = 29.999991 + 19.999984 + 9.998477 - 0.00522;$$

$$\therefore (60) = 59.993232 \quad . \quad . \quad . \quad . \quad J.$$

Again, adding i and j ,

$$(10) = 2(3) + (2) + 2(1) - 0.0005.$$

Multiplying k by 2,

$$2(3) = 2(2) + 2(1) + 0.0033.$$

Subtracting m from l ,

$$(2) = 2(1) + 0.00196.$$

Then $(i+j) + 2k + 3(l-m)$ gives

$$(10) + 10(1) + 0.00868;$$

$$\therefore 9.998477 = (10)1 + 0.00868;$$

$$\therefore 0.9998477 = (1) + 0.000868;$$

$$\therefore (1) = 0.9989797 \quad . \quad . \quad . \quad . \quad K.$$

From equation m we have

$$0.9989797 = (6) + (3) + (1) - 0.00508;$$

$$\therefore (6) + (3) + (1) = 1.0040597 \quad . \quad . \quad . \quad .$$

From l ,

$$(2) = 0.9989797 + 1.0040597 - 0.00312;$$

$$\therefore (2) = 1.9998894 \quad . \quad . \quad . \quad . \quad M.$$

From k ,

$$(3) = 1.9998894 + 0.9989797 + 0.00165;$$

$$\therefore (3) = 3.0004691 \quad . \quad . \quad . \quad . \quad N.$$

From j ,

$$(6) = 3.0004691 + 1.9998894 + 0.9989797 - 0.00102;$$

$$\therefore (6) = 5.9982682 \quad . \quad . \quad . \quad . \quad O.$$

Again, adding m and n ,

$$(1) = 2(3) + (2) + 2(1) - 0.00768.$$

Multiplying o by 2 we get

$$2(3) = 2(2) + 2(1) + 0.0045.$$

Subtracting q from p ,

$$(2) = 2(1) + 0.00702.$$

Then $(m+n) + 2o + 3(p-q)$ gives

$$(1) = 10(1) + 0.01788;$$

$$\therefore 0.9989797 = 10(1) + 0.01788;$$

$$\therefore 0.9989797 = (1) + 0.001788;$$

$$\therefore (1) = 0.99810997 \quad . \quad . \quad . \quad . \quad P.$$

From q we get

$$0.99810997 = (06) + (03) + (01) - 0.00802;$$

$$\therefore (06) + (03) + (01) = 0.10612997 \quad . \quad . \quad Q.$$

From p ,

$$(2) + 0.99810997 + 0.10612997 - 0.001;$$

$$\therefore (2) = 0.20823994 \quad . \quad . \quad . \quad . \quad R.$$

From o ,

$$(\cdot 3) = 0.20323994 + 0.09810997 + 0.00225; \\ \therefore (\cdot 3) = 0.30359991 \quad \text{S.}$$

From n we get

$$(\cdot 6) = 0.30359991 + 0.20323994 + 0.09810997 - 0.0026; \\ \therefore (\cdot 6) = 0.60234982 \quad \text{T.}$$

Again, adding q and r ,

$$(\cdot 1) = 2(\cdot 03) + (\cdot 02) + 2(\cdot 01) - 0.01409.$$

Multiplying s by 2 we get

$$2(\cdot 03) = 2(\cdot 02) + 2(\cdot 01) - 0.01284.$$

Subtracting u from t ,

$$(\cdot 2) = 2(\cdot 01) - 0.00531.$$

Then $(q + r) + 2s + 8(t - u)$ gives

$$(\cdot 1) = 10(\cdot 01) - 0.04286, \\ \therefore 0.09810997 = 10(\cdot 01) - 0.04286, \\ \therefore 0.009810997 = (\cdot 01) - 0.004286, \\ \therefore (\cdot 01) = 0.014096997 \quad \text{U.}$$

From u we get

$$0.014096997 = (\cdot 01r'') + 0.00413, \\ \therefore (\cdot 01r'') = 0.009966997 \quad \text{V.}$$

From t we get

$$(\cdot 02) = 0.014096997 + 0.009966997 - 0.00118, \\ \therefore (\cdot 02) = 0.022883994 \quad \text{W.}$$

From s we get

$$(\cdot 03) = 0.022883994 + 0.014096997 - 0.00642, \\ \therefore (\cdot 03) = 0.030560991 \quad \text{X.}$$

From r we get

$$(\cdot 06) = 0.030560991 + 0.22883994 + 0.014096997 - 0.00607, \\ \therefore (\cdot 06) = 0.061471982 \quad \text{Y.}$$

From v we get

$$0.014096997 = (\cdot 01r') + 0.0041, \\ \therefore (\cdot 01r') = 0.009996997 \quad \text{Z.}$$

The value of the weights thus given was, however, their weight in of the ordinary pressure; it became therefore necessary to ascertain their value in a vacuum. All bodies displace a bulk of air equal to their own volume, and the weight of this air is of course greater as their specific gravity diminishes. In delicate investigations this loss of weight is important. The reduction of the platinum weights to their true value *in vacuo* was calculated by the following formula:—

Let W = weight in air,

w = „ „ water,

a = specific gravity of air as compared with water;

then

$$x, \text{ or weight in } vacuo, = \frac{W - aw}{1 - a},$$

where

$$a = 0.001225, \text{ and}$$

$$1 - a = 0.998775.$$

The following Table shows the final results of these adjustments:—

Nominal Value of Weights	True Value in Air at 30 in. 63° F.	Weight of Air Displaced	Volume in Water of Maximum Density
gms.	gms.	gr.	gms.
1000-00	1000-000000	0-058271	47-5100
600-00	599-998340	0-035588	28-9700
300-00	300-000240	0-017501	14-2700
200-00	199-998910	0-011664	9-5100
100-00	99-991420	0-005887	4-8000
60-00	59-993232	0-003483	2-8400
30-00	29-999991	0-001668	1-3600
20-00	19-999984	0-001104	0-9000
10-00	9-998477	0-000490	0-4000
6-00	5-998268	0-000355	0-2900
3-00	3-000469	0-000171	0-1400
2-00	1-999839	0-000113	0-1000
1-00	0-998980	0-000055	0-0400
0-60	0-602350	0-000035	0-0300
0-30	0-303600	0-000017	0-0200
0-20	0-203240	0-000011	0-0100
0-10	0-098110	0-000005	0-0040
0-06	0-061472	0-000003	0-0030
0-03	0-030561	0-000002	0-0020
0-02	0-022884	0-000001	0-0010
0-01	0-014097	0-000001	0-0004
0-01'	0-009997	0-000001	0-0004
0-01"	0-009967	0-000001	0-0004

The value of each weight in air, plus the weight of air displaced, is the weight *in vacuo*.

Having ascertained their true value, the weights were carefully preserved; and as, being of platinum, there was no accumulation of tarnish on their surface, and as they were lifted with ivory-tipped forceps to prevent wear, they have shown up to the present time, whenever compared, absolutely no alteration.

¹ The cistern of the barometer is 115 feet above the approximate mean water-level at Somerset House.

CHAPTER XVI.

USEFUL TABLES.

Conversion of Centigrade and Fahrenheit Degrees.

$$1^{\circ}\text{C.} = 1.8^{\circ}\text{F.} = \frac{9}{5}^{\circ}\text{F.} \quad 1^{\circ}\text{C.} \times \frac{9}{5} = 1\text{F.} \quad 1^{\circ}\text{F.} \times \frac{5}{9} = 1^{\circ}\text{C.}$$

To convert Fahrenheit into Centigrade—Subtract 32 from the original number, and divide the remainder by 1.8, thus: $176^{\circ}\text{F.} - 32 + 1.8 = 80^{\circ}\text{Cent.}$

To convert Centigrade into Fahrenheit, multiply by 1.8, add 32 to the product, thus: $80^{\circ}\text{Cent.} \times 1.8 + 32 = 176^{\circ}\text{F.}$

With the aid of a scale like the accompanying one,¹ thermometric degrees may be converted from one to the other with the greatest accuracy without making any calculations.

A simple inspection of the diagram will suffice to show the principle upon which the scale is constructed. Each degree Fahrenheit is divided into 5 parts, and each degree Centigrade into 9 parts, which are intended to represent fractions of a degree; the degrees themselves being numbered consecutively from the freezing-point of each thermometer upwards.

A few examples will best explain the use of this scale. Suppose the temperature of a body to be 40°F. and it is required to know what degree that is on the Centigrade scale. By looking for the next degree Centigrade above 40°F. on the scale, it is found to be 4, and 4 of the small divisions after it; 40°F. are therefore equivalent to 4.4°C. , or, repeating the decimal figure for greater accuracy, 4.44°C.

When Centigrade degrees have to be reduced to degrees of Fahrenheit, the decimal figures of the latter must be doubled to obtain the correct answer. For example, it is required to represent 3°C. by their Fahrenheit equivalent; referring to the scale we find the next degree Fahrenheit above 3°C. to be 37.2° , and doubling the decimal figure we have the correct answer 37.4°F. Again, taking the outer columns of figures at the same place, we find 48°C. corresponding to 109.4°F.

¹ By Mr. Birney.

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FAHRENHEIT.				CENTIGRADE OR CELSIUS.			
140	104	68	32	0	20	40	60
141	105	69	33				
142	106	70	34	1	21	41	61
143	107	71	35				
144	108	72	36	2	22	42	62
145	109	73	37				
146	110	74	38	3	23	43	63
147	111	75	39				
148	112	76	40	4	24	44	64
149	113	77	41				
150	114	78	42	5	25	45	65
151	115	79	43				
152	116	80	44	6	26	46	66
153	117	81	45				
154	118	82	46	7	27	47	67
155	119	83	47				
156	120	84	48	8	28	48	68
157	121	85	49				
158	122	86	50	9	29	49	69
159	123	87	51				
160	124	88	52	10	30	50	70
161	125	89	53				
162	126	90	54	11	31	51	71
163	127	91	55				
164	128	92	56	12	32	52	72
165	129	93	57				
166	130	94	58	13	33	53	73
167	131	95	59				
168	132	96	60	14	34	54	74
169	133	97	61				
170	134	98	62	15	35	55	75
171	135	99	63				
172	136	100	64	16	36	56	76
173	137	101	65				
174	138	102	66	17	37	57	77
175	139	103	67				
				18	38	58	78
				19	39	59	79

Tables for the Mutual Conversion of French and English Weights and Measures.

The equivalents in one system of the weights and measures of the other system can readily be found by means of the following tables. By changing the position of the decimal point, the tables are available for all decimal multiples and subdivisions of these quantities; for instance, in order to find the part of a gramme which corresponds to 0.1, 0.01, 0.001, &c., of a grain, it is necessary to advance the decimal point one, two, or three places to the left. In the same manner it is advanced to the right for the purpose of finding the grammes corresponding to 10, 100, 1000, &c., grains.

For example:—In the table for the conversion of grammes into grains, it is required to find the equivalent in grains of 6·4431 grammes.

From number 6 (without altering the place of the decimal point)	92·6304
¹ From number 4 (advancing the decimal point one place to the left)	6·1753
¹ From number 4 (advancing the decimal point two places to the left)	0·6175
¹ From number 8 (advancing the decimal point three places to the left)	0·0463
¹ From number 1 (advancing the decimal point four places to the left)	0·0015
Therefore 6·4431 grammes are equal to	99·4710 grains.

Grammes into Grains.

Grammes	Grains	Grammes	Grains	Grammes	Grains
1 =	15·4384	4 =	61·7586	7 =	108·0688
2 =	30·8768	5 =	77·1920	8 =	123·5072
3 =	46·3152	6 =	92·6304	9 =	138·9456

Grains into Grammes.

Grains	Grammes	Grains	Grammes	Grains	Grammes
1 =	0·06477	4 =	0·25908	7 =	0·45339
2 =	0·12954	5 =	0·32385	8 =	0·51816
3 =	0·19431	6 =	0·38862	9 =	0·58293

Pounds into Kilogrammes.

Pounds	Kilogrammes	Pounds	Kilogrammes	Pounds	Kilogrammes
1 =	0·4534148	4 =	1·8136592	7 =	3·1739036
2 =	0·9068296	5 =	2·2670740	8 =	3·6273184
3 =	1·3602444	6 =	2·7204888	9 =	4·0807332

Kilogrammes into Pounds.

Kilogrammes	Pounds	Kilogrammes	Pounds	Kilogrammes	Pounds
1 =	2·205486	4 =	8·821944	7 =	15·438402
2 =	4·410972	5 =	11·027430	8 =	17·643888
3 =	6·616458	6 =	13·232916	9 =	19·849874

Inches into Centimetres.

Inches	Centimetres	Inches	Centimetres	Inches	Centimetres
1 =	2·539954	4 =	10·1598	7 =	17·7797
2 =	5·079900	5 =	12·6998	8 =	20·3196
3 =	7·619900	6 =	15·2397	9 =	22·8596

¹ In almost every case when the decimal point is moved to the left, the last figures may be omitted without introducing any appreciable error.

Centimetres into Inches.

Centimetres	Inches	Centimetres	Inches	Centimetres	Inches
1 =	0.3937079	4 =	1.5748316	7 =	2.7559553
2 =	0.7874158	5 =	1.9685395	8 =	3.1496632
3 =	1.1811287	6 =	2.3622474	9 =	3.5433711

Feet into Metres.

Feet	Metres	Feet	Metres	Feet	Metres
1 =	0.3047945	4 =	1.2197680	7 =	2.1336614
2 =	0.6095890	5 =	1.5239724	8 =	2.4383559
3 =	0.9143835	6 =	1.8287669	9 =	2.7431504

Metres into Feet.

Metres	Feet	Metres	Feet	Metres	Feet
1 =	3.2808992	4 =	13.1235968	7 =	22.9662944
2 =	6.5617984	5 =	16.4044960	8 =	26.2471986
3 =	9.8426976	6 =	19.6853952	9 =	29.5280928

Miles into Kilometres.

Miles	Kilometres	Miles	Kilometres	Miles	Kilometres
1 =	1.6093	4 =	6.4373	7 =	11.2652
2 =	3.2186	5 =	8.0466	8 =	12.8745
3 =	4.8279	6 =	9.6559	9 =	14.4838

Kilometres into Miles.

Kilometres	Miles	Kilometres	Miles	Kilometres	Miles
1 =	0.62138	4 =	2.48552	7 =	4.34966
2 =	1.24276	5 =	3.10690	8 =	4.97104
3 =	1.86414	6 =	3.72828	9 =	5.59242

Square Feet into Square Metres.

Sq. Feet	Sq. Metres	Sq. Feet	Sq. Metres	Sq. Feet	Sq. Metres
1 =	0.0929	4 =	0.3716	7 =	0.6503
2 =	0.1858	5 =	0.4645	8 =	0.7432
3 =	0.2787	6 =	0.5574	9 =	0.8361

Square Metres into Square Feet.

Sq. Metres	Sq. Feet	Sq. Metres	Sq. Feet	Sq. Metres	Sq. Feet
1 =	10.7639	4 =	43.0792	7 =	75.3886
2 =	21.5896	5 =	53.8490	8 =	86.1584
3 =	32.3094	6 =	64.6188	9 =	96.9282

Cubic Feet into Cubic Metres.

Cub. Feet	Cub. Metres	Cub. Feet	Cub. Metres	Cub. Feet	Cub. Metres
1 =	0.028314	4 =	0.113256	7 =	0.198198
2 =	0.056628	5 =	0.141570	8 =	0.226512
3 =	0.084942	6 =	0.169884	9 =	0.254826

Cubic Metres into Cubic Feet.

Cub. Metres	Cub. Feet	Cub. Metres	Cub. Feet	Cub. Metres	Cub. Feet
1 =	35·8171	4 =	141·2684	7 =	247·2197
2 =	70·6342	5 =	176·5855	8 =	282·5368
3 =	105·9513	6 =	211·9026	9 =	317·8539

Long Tons into Tonnes of 1000 Kilos.

Long Tons	Tonnes of 1000 Kilos.	Long Tons	Tonnes of 1000 Kilos.	Long Tons	Tonnes of 1000 Kilos.
1 =	1·015649	4 =	4·062596	7 =	7·109543
2 =	2·031298	5 =	5·078245	8 =	8·125192
3 =	3·046947	6 =	6·093894	9 =	9·140841

Pounds per Square Inch into Kilogrammes per Square Centimetre.

Pounds per Sq. Inch	Kilos. per Sq. Centim.	Pounds per Sq. Inch	Kilos. per Sq. Centim.	Pounds per Sq. Inch	Kilos. per Sq. Centim.
1 =	0·0702774	4 =	0·2811096	7 =	0·4919418
2 =	0·1405548	5 =	0·3513870	8 =	0·5622192
3 =	0·2108322	6 =	0·4216644	9 =	0·6324966

Kilogrammes per Square Millimetre into Pounds per Square Inch.

Kilos. per Sq. Millim.	Pounds per Sq. Inch	Kilos. per Sq. Millim.	Pounds per Sq. Inch	Kilos. per Sq. Millim.	Pounds per Sq. Inch
1 =	1425·45	4 =	5701·80	7 =	6978·15
2 =	2850·90	5 =	7127·25	8 =	11408·60
3 =	4276·35	6 =	8552·70	9 =	12829·05

Relative Values of French and English Weights and Measures.**WEIGHTS.**

Milligramme	=	0·015438895	troy grain
Centigramme	=	0·154388395	" "
Decigramme	=	1·54388395	" "
Gramme	=	15·4388395	" "
"	=	0·648	pennyweight
"	=	0·08216	oz. troy
"	=	0·03527	oz. avoirdupois
Decagramme	=	154·388395	troy grains
"	=	5·64	drams avoirdupois
Hectogramme	=	3·2154	ozs. troy
"	=	3·527	ozs. avoirdupois
Kilogramme	=	2·6803	lbs. troy
"	=	2·205486	lbs. avoirdupois
Myriagramme	=	26·803	lbs. troy
"	=	22·05486	lbs. avoirdupois
Quintal metrique	=	100 kilos.	= 220·5486 lbs. avoir.
Tonne	=	1000 "	= 2205·486 "

Different authors give the following values for the gramme :—

Gramme	=	15·44402	troy grains
"	=	15·44242	"
"	=	15·4402	"
"	=	15·438159	"
"	=	15·43235	"

Avoirdupois.

Long ton = 20 cwt. = 2240 lbs.	=	1015·649	kilogrammes
Short ton (2000 lbs.)	.	.	= 906·8296 "
Hundredweight (112 lbs.)	.	=	50·78245 "
Quarter (28 lbs.)	.	.	= 12·6956144 "
Pound = 16 ozs.	=	7000 grs.	= 453·4148 grammes
Ounce = 16 drams	=	437·5 grs.	= 28·3375 "
Dram = 27·344 grains	=	1·77108	gramme
Grain	.	.	= 0·064773 "

Troy (Precious Metals).

Pound = 12 ozs.	=	5760 grs.	= 373·096 grammes
Ounce = 20 dwts.	=	480 "	= 31·0913 "
Pennyweight.	=	24 "	= 1·55457 gramme
Grain	.	.	= 0·064773 "

Troy (Pharmacy).

Ounce = 8 drams	=	480 grs.	= 31·0913 grammes
Dram = 8 scruples	=	60 "	= 3·8869 "
Scruple = .	.	= 20 "	= 1·29546 gramme

MEASURES OF LENGTH.

Millimetre	=	0·08937	inch
Centimetre	=	0·393708	"
Decimetre	=	3·937079	inches
Metre	=	39·37079	"
"	=	3·2808992	feet
"	=	1·093683	yard
Inch ($\frac{1}{36}$ th yard)	.	.	= 2·539954 centimetres
Foot ($\frac{1}{3}$ rd yard)	.	.	= 3·0479449 decimetres
Yard.	.	.	= 0·91438348 metre
Mile (1760 yards)	.	.	= 1609·3149 metres

SUPERFICIAL MEASURES.

Square millimetre	.	.	.	=	$\frac{1}{645}$ th of a square inch
"	"	.	.	=	0·00155 " "
" centimetre	.	.	.	=	0·155086 " "
" decimetre	.	.	.	=	15·5086 " inches
"	.	.	.	=	0·10769 " foot
" metre or centiare	.	.	.	=	1550·86 " inches
"	"	.	.	=	10·7698 " feet
"	"	.	.	=	1·196033 " yard

Are	=	1076.98	„ feet
„	=	119.6083	„ yards
„	=	0.098845	„ rood
Hectare	=	11960.33	„ yards
„	=	2.471143	„ acres
Square inch	=	645.109201	„ millimetres
„	=	6.45109	„ centimetres
„ foot	=	9.2903	„ decimetres
„ yard	=	0.836097	„ metre
Acre (4840 square yards)	=	0.404671	„ hectare

MEASURES OF CAPACITY.

Cubic millimetre	=	0.000061029	cubic inch
„ centimetre	=	0.061029	„ „
10 cubic centimetres	=	0.61029	„ „
100 „ „	=	6.10295	„ inches
1000 „ „ or litre	=	61.0295688	„ „
„ „ „	=	1.760773	imperial pint
„ „ „	=	0.2200967	„ gallon
Decalitre	=	610.295688	cubic inches
„	=	2.2009668	imp. gallons
Hectolitre	=	8.5317	cubic feet
„	=	22.009668	imp. gallons
Cubic metre	=	1.308	cubic yard
„ „	=	35.3171	„ feet
Cubic inch = 16.3855			cubic centimetres
„ foot = 28.3159			„ decimetres
„ yard = 0.764520696			„ metre

BRITISH IMPERIAL MEASURES.

Pint ($\frac{1}{8}$ gallon)	=	0.567982	litre
Quart ($\frac{1}{4}$ „)	=	1.135964	„
Imperial gallon	=	4.54845797	litres

WEIGHT OF WATER, &c.

1 cubic inch	252.45	grs.
1 pint (= 34.65 cubic inches)	1.25	lb.
1 cubic foot (= 6.25 galls., or 1000 ozs.)	62.50	lbs.
1 gallon (= 277.274 cubic inches)	10.00	lbs.
1.8 cubic foot	1	cwt.
35.84 cubic feet	1	ton.
11.20 gallons	1	cwt.
224.0 „	1	ton.
A cubic inch of mercury = 3425.25 grains.		

Baumé's Hydrometer.

The following tables give the comparison of the degrees of Baumé's hydrometer with the specific gravity :—

Table for Liquids Heavier than Water.

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
0	1.000	26	1.206	52	1.520
1	1.007	27	1.216	53	1.535
2	1.013	28	1.226	54	1.551
3	1.020	29	1.236	55	1.567
4	1.027	30	1.246	56	1.583
5	1.034	31	1.256	57	1.600
6	1.041	32	1.267	58	1.617
7	1.048	33	1.277	59	1.634
8	1.056	34	1.288	60	1.652
9	1.063	35	1.299	61	1.670
10	1.070	36	1.310	62	1.689
11	1.078	37	1.322	63	1.708
12	1.086	38	1.333	64	1.727
13	1.094	39	1.345	65	1.747
14	1.101	40	1.357	66	1.767
15	1.109	41	1.369	67	1.788
16	1.118	42	1.382	68	1.809
17	1.126	43	1.395	69	1.831
18	1.134	44	1.407	70	1.854
19	1.143	45	1.421	71	1.877
20	1.152	46	1.434	72	1.900
21	1.160	47	1.448	73	1.924
22	1.169	48	1.462	74	1.949
23	1.178	49	1.476	75	1.974
24	1.188	50	1.490	76	2.000
25	1.197	51	1.505		

Table for Liquids Lighter than Water.

Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity	Degrees Baumé	Specific Gravity
10	1.000	27	0.896	44	0.811
11	0.993	28	0.890	45	0.807
12	0.986	29	0.885	46	0.802
13	0.980	30	0.880	47	0.798
14	0.973	31	0.874	48	0.794
15	0.967	32	0.869	49	0.789
16	0.960	33	0.864	50	0.785
17	0.954	34	0.859	51	0.781
18	0.948	35	0.854	52	0.777
19	0.942	36	0.849	53	0.773
20	0.936	37	0.844	54	0.768
21	0.930	38	0.839	55	0.764
22	0.924	39	0.834	56	0.760
23	0.918	40	0.830	57	0.757
24	0.913	41	0.825	58	0.753
25	0.907	42	0.820	59	0.749
26	0.901	43	0.816	60	0.745

Twaddell's Hydrometer.

To convert degrees of Twaddell's hydrometer into specific gravity, multiply the number by 5, and add 1000 to the product.

Example.

25 Twaddell $\times 5 + 1000 = 1125$ specific gravity.

To reduce specific gravity into degrees Twaddell, deduct 1000 from the number, and divide the remainder by 5.

Example.

Specific gravity 1125 $- 1000 \div 5 = 25$ Twaddell.

Percentage of Soda in Aqueous Solutions of Various Specific Gravities.

Temp. 15°.

Specific Gravity	Na ₂ O. p.c.	Specific Gravity	Na ₂ O. p.c.	Specific Gravity	Na ₂ O. p.c.
1.015	1	1.190	13	1.355	25
1.020	2	1.203	14	1.369	26
1.043	3	1.219	15	1.381	27
1.058	4	1.233	16	1.395	28
1.074	5	1.245	17	1.410	29
1.089	6	2.258	18	1.422	30
1.104	7	1.270	19	1.438	35
1.119	8	1.285	20	1.558	40
1.132	9	1.300	21	1.623	45
1.145	10	1.315	22	1.690	50
1.160	11	1.329	23	1.760	55
1.175	12	1.341	24	1.830	60

Percentage of Caustic Potash in Aqueous Solutions of Various Specific Gravities.

Temp. 15°.

Specific Gravity	K ₂ O. p.c.	Specific Gravity	K ₂ O. p.c.	Specific Gravity	K ₂ O. p.c.
1.0050	0.5658	1.1182	11.882	1.30	29.34
1.0153	1.6970	1.1437	14.145	1.34	32.14
1.0260	2.8290	1.1702	16.408	1.38	34.74
1.0369	3.9610	1.1979	18.671	1.42	37.97
1.0478	5.0020	1.2268	20.935	1.46	42.31
1.0589	6.2240	1.2493	22.632	1.50	46.45
1.0703	7.3550	1.2805	24.895	1.54	50.09
1.0819	8.4870	1.3131	27.158	1.58	53.06
1.0938	9.6190				

*Percentage of Ammonia in Aqueous Solutions of Various
Specific Gravities.*

Temp. 14°.

Specific Gravity	NH ₃ p.c.	Specific Gravity	NH ₃ p.c.	Specific Gravity	NH ₃ p.c.
·8844	36	·9133	24	·9520	12
·8864	35	·9162	23	·9556	11
·8885	34	·9191	22	·9593	10
·8907	33	·9221	21	·9631	9
·8929	32	·9251	20	·9670	8
·8953	31	·9283	19	·9709	7
·8976	30	·9314	18	·9749	6
·9001	29	·9347	17	·9790	5
·9026	28	·9380	16	·9831	4
·9052	27	·9414	15	·9873	3
·9078	26	·9449	14	·9915	2
·9106	25	·9484	13	·9959	1

*Percentage of Nitric Acid in Aqueous Solutions of Various
Specific Gravities.*

Temp. 15°.

Specific Gravity	HNO ₃ p.c.	Specific Gravity	HNO ₃ p.c.	Specific Gravity	HNO ₃ p.c.
1·010	2·00	1·225	36·00	1·429	71·24
1·022	4·00	1·251	40·00	1·438	74·01
1·045	7·22	1·274	43·53	1·451	77·66
1·067	11·41	1·298	47·18	1·463	80·96
1·077	13·00	1·323	50·99	1·474	84·00
1·089	15·00	1·339	53·81	1·482	86·17
1·105	17·47	1·353	56·10	1·494	89·56
1·120	20·00	1·372	59·59	1·506	93·01
1·138	23·00	1·381	61·21	1·514	95·27
1·166	27·00	1·400	65·07	1·523	97·89
1·185	30·00	1·410	67·00	1·530	99·72
1·211	33·86	1·419	69·20	1·530	100·00

Percentage of Sulphuric Acid in Aqueous Solutions of Various Specific Gravities.

Temp. 15°.

Specific Gravity	H ₂ SO ₄ p.c.	Specific Gravity	H ₂ SO ₄ p.c.	Specific Gravity	H ₂ SO ₄ p.c.
1.0064	1	1.1060	15	1.2890	38
1.0130	2	1.1186	16	1.3060	40
1.0190	3	1.1210	17	1.3510	45
1.0256	4	1.1290	18	1.3980	50
1.0320	5	1.1360	19	1.4480	55
1.0390	6	1.1440	20	1.5010	60
1.0464	7	1.1590	22	1.5570	65
1.0536	8	1.1740	24	1.6150	70
1.0610	9	1.1900	26	1.6750	75
1.0680	10	1.2066	28	1.7340	80
1.0756	11	1.2230	30	1.7860	85
1.0830	12	1.2390	32	1.8220	90
1.0910	13	1.2560	34	1.8376	95
1.0980	14	1.2720	36	1.8426	100

Percentage of Hydrochloric Acid in Aqueous Solutions of Various Specific Gravities.

Temp. 15°.

Specific Gravity	HCl. p.c.	Specific Gravity	HCl. c.p.	Specific Gravity	HCl. p.c.
1.0020	0.408	1.0637	13.049	1.1802	36.292
1.0040	0.816	1.0738	15.087	1.1846	37.108
1.0060	1.124	1.0818	16.718	1.1857	37.516
1.0100	2.039	1.0899	18.349	1.1875	37.923
1.0140	2.854	1.1000	20.888	1.1893	38.330
1.0180	3.670	1.1143	23.242	1.1910	38.738
1.0220	4.486	1.1287	26.098	1.1928	39.146
1.0279	5.709	1.1410	28.544	1.1946	39.554
1.0337	6.932	1.1515	30.582	1.1964	39.961
1.0397	8.155	1.1641	33.029	1.1982	40.369
1.0457	9.379	1.1741	35.068	1.2000	40.777
1.0557	11.418				

Atomic Weights of the Elements.¹

Name	Symbol	Atomic Weight	Name	Symbol	Atomic Weight
Aluminium . . .	Al	27.01	Molybdenum . . .	Mo	95.53
Antimony . . .	Sb	119.95	Nickel . . .	Ni	57.93
Arsenic . . .	As	74.92	Nitrogen . . .	N	14.02
Barium . . .	Ba	136.76	Osmium . . .	Os	198.49
Bismuth . . .	Bi	207.52	Oxygen . . .	O	15.963
Boron . . .	Bo	10.94	Palladium . . .	Pd	105.73
Bromine . . .	Br	79.77	Phosphorus . . .	P	30.96
Cadmium . . .	Cd	111.83	Platinum . . .	Pt	194.41
Cæsium . . .	Cs	132.58	Potassium . . .	K	39.02
Calcium . . .	Ca	39.99	Rhodium . . .	Rh	104.05
Carbon . . .	C	11.97	Rubidium . . .	Rb	85.25
Cerium . . .	Ce	140.42	Ruthenium . . .	Ru	104.22
Chlorine . . .	Cl	35.37	Samarium . . .	Sm	149.80
Chromium . . .	Cr	52.01	Scandium . . .	Sc	43.98
Cobalt . . .	Co	58.88	Selenium . . .	Se	78.79
Columbium . . .	Nb	93.81	Silicon . . .	Si	28.19
Copper . . .	Cu	63.17	Silver . . .	Ag	107.67
Didymium . . .	Di	142.12	Sodium . . .	Na	22.99
Erbium . . .	Er	165.89	Strontium . . .	Sr	87.87
Fluorine . . .	F	18.98	Sulphur . . .	S	31.98
Gallium . . .	Ga	68.85	Tantalum . . .	Ta	182.14
Glucinum . . .	Gl	9.08	Tellurium . . .	Te	127.96
Gold . . .	Au	196.15	Thallium . . .	Tl	208.71
Hydrogen . . .	H	1.00	Thorium . . .	Th	233.41
Indium . . .	In	113.89	Tin . . .	Sn	117.69
Iodine . . .	I	126.55	Titanium . . .	Ti	47.98
Iridium . . .	Ir	192.65	Tungsten . . .	W	183.61
Iron . . .	Fe	55.91	Uranium . . .	U	238.48
Lanthanum . . .	La	138.02	Vanadium . . .	V	51.25
Lead . . .	Pb	206.47	Ytterbium . . .	Yb	172.76
Lithium . . .	Li	7.01	Yttrium . . .	Yt	88.90
Magnesium . . .	Mg	23.96	Zinc . . .	Zn	64.90
Manganese . . .	Mn	53.90	Zirconium . . .	Zr	89.36
Mercury . . .	Hg	199.71			

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